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"Living" Free Radical Photopolymerization Initiated from Surface-Grafted Iniferter Monolayers

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ABSTRACT: A method for chemically modifying a surface with grafted monolayers of initiator groups, which can be used for a "living" free radical photopolymerization, is described. By using "living" free radical polymerizations, we were able to control the length of the grafted polymer chains and therefore the layer thickness up to ~ 100 nm. Also, single-layer grafted block copolymers were obtained by subsequent polymerizations of styrene and methyl methacrylate monomers. The surface-grafted polymer and block copolymer layers were evidenced by direct imaging methods (transmission and scanning electron microscopy) and by indirect surface characterization methods (contact angle measurements, SFM, XPS, and IR). The ability to control the thickness of the grafted polymer as well as the synthesis of a grafted block copolymer layer in a well-defined manner affirms the "living" character of the surface-initiated free radical photopolymerization.

Introduction

Modification of surfaces of solid (in)organic materials is often utilized to change properties such as biocompatibility, wetting, adhesion, or friction. Modifications with polymer layers are recognized to play an important role, especially in printing, coating, food packaging, microelectronics, biomedical, and aerospace applications. Engineering surfaces at a molecular level gained interest during the 1990s, because this can lead to well-defined surfaces with better macroscopic properties than those obtained by coating the surface with a thin (functional) polymer film. Coating of surfaces by irreversible grafting of a stable, preformed polymer¹ or by selective adsorption of a diblock copolymer² leads, in general, to nonuniform thin films and poor surface coverage, due to the formation of islands and mushrooms on the surface. Other frequently used methods such as polyelectrolyte deposition,³ plasma deposition,⁴ and polymerization within a Langmuir-Blodgett (LB) film suffer from the same disadvantages. Furthermore, these techniques do not completely control the growth of stable polymer films at the nanoscale level, which is required for most of the applications.

To overcome this, direct initiation of a polymer chain from a surface can be applied, which is expected to lead to higher surface grafting densities, because monomers can more easily diffuse toward the reactive center, whereas grafting or selective adsorption of polymers is limited by steric and entropic forces.

The autoassociation process has been used for covalently attaching a monolayer with high grafting densities on a surface. Examples of this are alkanethiols, which are known to form very stable monolayers on gold,⁵ and alkoxy silanes, which are used to modify solid

surfaces such as glass, silicon wafers, quartz, and mica. At these surfaces, the alkoxy silane group is converted to a stable poly(siloxane) layer by coupling with the free hydroxyl groups on the surface.

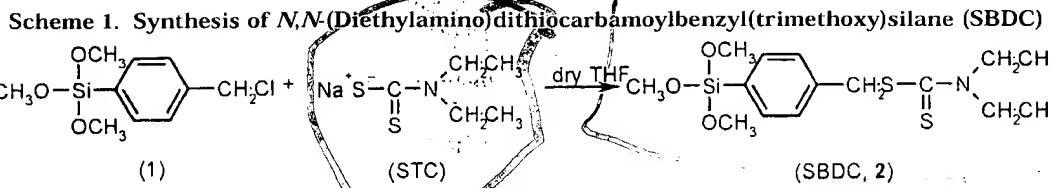
To initiate a polymerization from the surface, the autoassociating molecule had to be modified with an initiator group. In most cases, conventional radical initiating species^{6,7} or ionic moieties^{8,9} are introduced on the surface. For the polymerization of block copolymers and for controlling the molecular weight, and thus layer thickness as well as the composition, one is restricted to using the "living" polymerization technique.

Advanced "living" free radical polymerization methods allow the synthesis of a wide variety of macromolecules with monomers that cannot be polymerized with the traditional cationic and anionic living polymerizations.^{9,10} Three "living" free radical polymerization methods are often employed, namely the atom transfer radical polymerization (ATRP),¹¹ the nitroxide-mediated free radical polymerization (TEMPO),¹² and the polymerization method based on iniferters.¹³ In this study we used the photoiniferter technique explored by Otsu et al.¹⁴ in the early 1980s. The concept of these nonconventional initiators is based on the formation of a reactive radical and a relatively stable counter radical, where the latter does not participate in the initiation, but merely acts as a transfer agent and terminating species (*iniferter*). The advantages of "living" free radical polymerizations are (a) linear increase of molecular weight with time, leading to a steady growth of the uniform polymer layer on the surface, (b) possibility of the formation of block copolymers by reinitiating the polymerization in a different monomer solution, and (c) compatibility with a wide variety of monomers, e.g., acrylates, styrenes, acrylonitrile, and derivatives. Furthermore, in the particular case of surface-initiated "living" free radical polymerizations, the preparation and handling of the samples are easier,¹⁷ which allows one to characterize the surface between two subsequent polymerizations.

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Just recently, three papers on controlled radical polymerization initiated by a surface-grafted initiator appeared.^{15–17} In the first two papers, the authors used atom transfer radical polymerization (ATRP) to control the molecular weight and thereby the layer thickness. A disadvantage of this method is the presence of inorganic salts at the surface, which would require further purification steps. The third paper, by Husselman and co-workers,¹⁷ deals with 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO)-functionalized chlorosilanes for the modification of the surface. The authors obtained an accurate control of molecular weight (or layer thickness) and were able to polymerize sequentially different monomers to obtain block copolymers, which is one of the ultimate goals in this field of research.

Other groups^{18,19} used grafted iniferter on the surface of silica gel, which resulted in difficulties regarding the characterization of the initiator monolayer formed and of the thickness of the polymer layer on the surface. Kobayashi and co-workers¹⁹ grafted *N,N*(diethylamino)dithiocarbamoylpropyl(trimethoxy)silane on a glass surface and initiated the photopolymerization of sodium styrenesulfonate from the surface, but a controlled radical polymerization could not be obtained, which corresponds to results found in the literature.²⁰ Nakayama, Matsuda, and co-workers used thin polymeric films partially derivatized with *N,N*-diethyldithiocarbamate groups and characterized the different grafted polymer layers with scanning force microscopy (SFM).²¹ In this case the growing polymer chain is not directly bound to the (inorganic) substrate. The authors were able to obtain a patterned surface by applying a striped projection mask, which is an advantage of photopolymerizations.

In our work, initially we modified the surface with thiol-functionalized iniferters, since thiol-terminated molecules are known to form thermally stable bound monolayers on a gold surface,²² and moreover these molecules can undergo chemical modification in such a layer similar to the reactions in solution.²³ Unfortunately, the thiol–gold bond proved to be unstable toward UV irradiation,²⁴ and therefore organosilane-terminated iniferters were used to graft the iniferter monolayer on silicon wafers and glass. The iniferter monolayers were used for the surface-initiated photopolymerizations of styrene (St) and methyl methacrylate (MMA) into homopolymers and block copolymers. In the case of block copolymerization of PS-*b*-PMMA, the macroinitiator efficiency is found to be less than in the photopolymerization of styrene. Furthermore, the photolysis of the dithiocarbamate end group and other side reactions in the MMA polymerization are known to play an important role in solution photopolymerizations.²⁵ In our case, however, due to the “confined two-dimensional” character of the photopolymerization, the efficiency may be improved and side reactions limited.

We used surfaces with chromium lines as a reference and for the facile direct visualization and measurement of the growing polymer layer with SFM. Furthermore, we used scanning electron microscopy (SEM), transmis-

sion electron microscopy (TEM), contact angles, IR, and X-ray photoelectron spectroscopy (XPS) for providing both direct and indirect evidence for the presence of the polymer layer on the substrates.

In this paper we describe the formation of densely grafted stable alkoxy silane monolayers modified with iniferter end groups and the “living” free radical photopolymerizations of styrene and methyl methacrylate into homopolymers and block copolymers initiated from these monolayers.

Experimental Section

Materials. *p*-(Chloromethyl)phenyltrimethoxysilane (ABCR), ethanol, chloroform (Labscan), and dichloromethane (Aldrich) were used as received. Prior to use, sodium *N,N*-diethyldithiocarbamate (Aldrich) was recrystallized from methanol, THF was distilled from potassium, and toluene was distilled from sodium/benzophenone. Water was deionized (18.2 MΩ·cm resistivity) with a Millipore Milli-Q filtration system. Styrene (Acros) and methyl methacrylate (Merck) were distilled at reduced pressure prior to use.

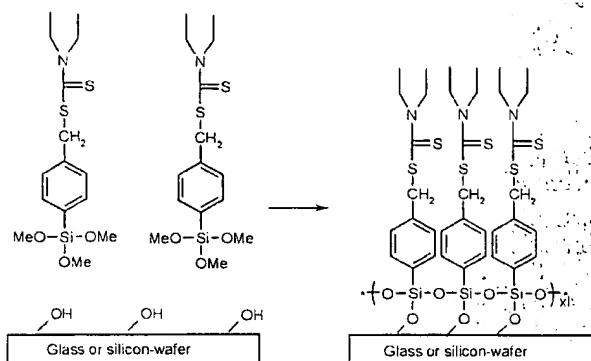
Synthesis of Silane-Terminated Iniferter (SBDC). *p*-(Chloromethyl)phenyltrimethoxysilane (1) (1.48 g, 6 mmol) and sodium *N,N*-diethyldithiocarbamate (STC) (1.02 g, 6 mmol) were each dissolved separately in 10 mL of dry THF (Scheme 1). The STC solution was added slowly to (1) via a syringe. The solution was stirred for 3 h at room temperature. A white precipitate was formed almost immediately (NaCl), and during the reaction period the solution became more yellow. The precipitate was removed by filtration through a glass filter. The THF was evaporated, and a yellow viscous liquid remained, which was vacuum-distilled in a Kugelrohr (160 °C, 0.1 mbar). The product *N,N*(diethylamino)dithiocarbamoylbenzyl(trimethoxy)silane (2) (SBDC) was obtained as a light-yellow viscous liquid, 0.638 g (yield: 30%). By synthesizing SBDC in bulk instead of on the surface, one can purify and characterize the initiating species by ¹H NMR. SBDC (2) proved to be stable (¹H NMR) for months in bulk or solution when kept cool and in the dark.

¹H NMR (CDCl₃): δ 7.65–7.38 (dd, 4H, C₆H₄, *J* = 6.5 Hz), 4.55 (s, 2H, CH₂S), 4.05 (q, 2H, NCH₂, *J* = 6.7 Hz), 3.73 (q, 2H, NCH₂, *J* = 6.7 Hz), 3.62 (s, 9H, Si(OCH₃)₃), 1.25 (t, 6H, CH₃, *J* = 7.0 Hz).

Grafting of Silane-Terminated Iniferter (SBDC) on Silicon. The Si wafers (or similar substrates) were rinsed with water and then sonicated for 15 min in water. This procedure was repeated with ethanol and followed by rinsing in refluxing CH₂Cl₂ for 15 min. To break the Si–O bonds on the surface, a solution of hydrogen peroxide, ammonia (25%), and water (H₂O₂:NH₃:H₂O, 1:1:5) was prepared and heated to about 70 °C, and the wafers were added to the mixture for 10 min. After thorough rinsing with water, they were immersed in a solution of hydrochloric acid (HCl:H₂O, 1:6) for 30 min at room temperature.²⁶ The wafers were rinsed with water, ethanol, and THF or toluene depending on the solvent used for the monolayer formation.

The freshly prepared wafers were placed directly in a 1–5 mM solution of SBDC (2) in THF or toluene overnight at room temperature (Scheme 2), rinsed with toluene, and dried under a dry-prepurified N₂ flow.

“Living” Free Radical Photopolymerization Initiated by SBDC. A clean and oven-dry reaction tube was purged with argon. Under an argon flow, 7 mL of distilled monomer (styrene or MMA), 2.5 mL of dry toluene, and the samples,

Scheme 2. Idealized Presentation of the SBDC Monolayer on Silicon Wafers or Glass

grafted with the iniferter moiety, were added to the tube. The tube was placed at about 10 cm from a 365 nm TQ-150[°] UV-lamp (150 W) and irradiated for the required time at room temperature. After polymerization, the samples were submerged in 20 mL of dry toluene and sonicated for at least 10 min to remove homopolymer that may have been formed in solution and adheres to the surface. Finally, the surface was dried under a prepurified N₂ flow and kept in a sealed tube under N₂ until further use. The samples were characterized with SFM and subsequently used in blocking experiments with MMA. For the latter, the samples were submerged in 2.5 mL of dry toluene, and 7 mL of distilled MMA was added. The same procedure as described above was utilized. After the photopolymerization of the second block, the samples were submerged in 20 mL of dry toluene, sonicated for at least 10 min, and washed with toluene.

In other characterizations (IR, contact angle, SEM, and TEM) multiple samples, all prepared in one batch, were used. The samples were taken out of the solution after the required polymerization time, washed with dry toluene, submerged in dry toluene, and sonicated for at least 10 min. One sample was used for characterization, whereas the other samples were submerged in dry toluene and monomer for the consecutive photopolymerization.

Analysis. Fourier transformed ¹H NMR spectra were recorded in CDCl₃ on a Varian Gemini-200 spectrometer working at 200 MHz with chloroform as internal reference at 7.24 ppm. TEM pictures of 80 nm thick cross sections, which were deposited on a TEM grid, were taken using a JEOL EM 1200-EX microscope working at 100 kV. Scanning electron microscopy pictures were taken using a JEOL 6320F field emission microscope. Scanning force microscopy images were recorded with a Topometrix Discoverer TMX 2010, equipped with a Si₃N₄ tip. Topographic images were taken in air at a force of about 10 nN in contact mode.

Transmission IR spectra were recorded on a Mattson IR spectrometer. X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Surface Science SSX-100, using Mg K α excitation, and contact angles were measured on a home-built apparatus²⁷ as advancing water contact angles.

Results and Discussion

Grafting of Silane-Terminated Iniferter (SBDC) on Silicon and Subsequent Photopolymerization.

The formation of the SBDC monolayer on silicon wafers and glass was investigated by measuring the contact angles of the clean and modified substrate (Table 1). Silicon wafers have typical water contact angles around 10°; when the Si surface is cleaned with organic solvents, however, slightly higher contact angles are obtained. The SBDC-modified Si surface shows a considerable hydrophobic effect as can be seen by the high contact angle of 80 ± 5° (Table 1).

Table 1. Advancing Contact Angles of Water in Air for Cleaned and Modified Si Wafers

surface	measd angle (deg)	lit. values ²⁸ (deg)
cleaned Si wafer	16 ± 2	10–20
Si wafer modified with a monolayer of SBDC	80 ± 5	unknown
Si wafer after surface-grafted homopolymerization of St (15 h)	87 ± 3	87
Si wafer after surface-grafted block copolymerization of PS- <i>b</i> -PMMA (15 h)	66 ± 3	76

Further investigations of the SBDC-modified surfaces were done by XPS. In Figure 1 the XPS spectrum for the SBDC monolayer on a silicon wafer (Figure 1B) is given, together with a reference spectrum of cleaned silicon (Figure 1A). The strong silicon peaks of the substrate overlap with the sulfur peak of SBDC, and a small nitrogen peak (at 400 eV) is observed. Also, the carbon peak at 285 eV has increased, indicating the presence of the SBDC moiety. The ratio of the carbon and nitrogen peak areas is roughly in accordance with that expected on the basis of the molar ratio between these atoms in the SBDC monolayer.

The "living" free radical polymerization of styrene (St) and methyl methacrylate (MMA) at the SBDC modified Si surface yielded the grafted polystyrene (Si-PS) and poly(methyl methacrylate) (Si-PMMA) layers, respectively, on the Si surface.

The value for the contact angle of the polystyrene surface is in good agreement with the value found in the literature,²⁸ while the PMMA angle was found to be about 10° lower in most cases. The reason for this difference is not clear, but one has to consider that the literature values are determined on surfaces of PMMA bulk samples. In our case, however, we have a grafted PMMA layer with initiator end groups. Also, large differences in contact angles may originate from inhomogeneities in the very thin grafted polymer layer.

As expected, the contact angle measurements demonstrate that both polymer layers are hydrophobic. The acrylate groups of PMMA result in a significantly lower contact angle than PS (Table 1), enough to distinguish between a polystyrene layer and a poly(methyl methacrylate) layer. Thus, the contact angle measurements can be used to follow the growth of polymer bilayers upon reinitiation of the polymerization with a second monomer. The contact angle measurements, before and after the initiation of the second monomer, show qualitative changes in hydrophobicity in the same order as found upon switching from a polystyrene to a poly(methyl methacrylate) surface. The merely qualitative nature of the contact angle measurements prevents an unambiguous characterization of the surface-initiated polymer layers. Hence, transmission IR spectroscopy (TIR) was used to confirm the results of the grafted polystyrene on silicon. The wafers were about 1 × 1 cm² and 1 mm thick. The spectra are depicted in Figure 2. For each measurement 1000 scans were made. Water peaks were subtracted by using a reference spectrum. The first sample was measured directly after deposition of the iniferter monolayer. The other two samples were measured after photopolymerization of styrene for 4 and 10 h, respectively. The photopolymerized polystyrene samples show the typical peaks for polystyrene surfaces, as can be seen from the reference spectrum (bottom). The increasing intensity of the signals after longer

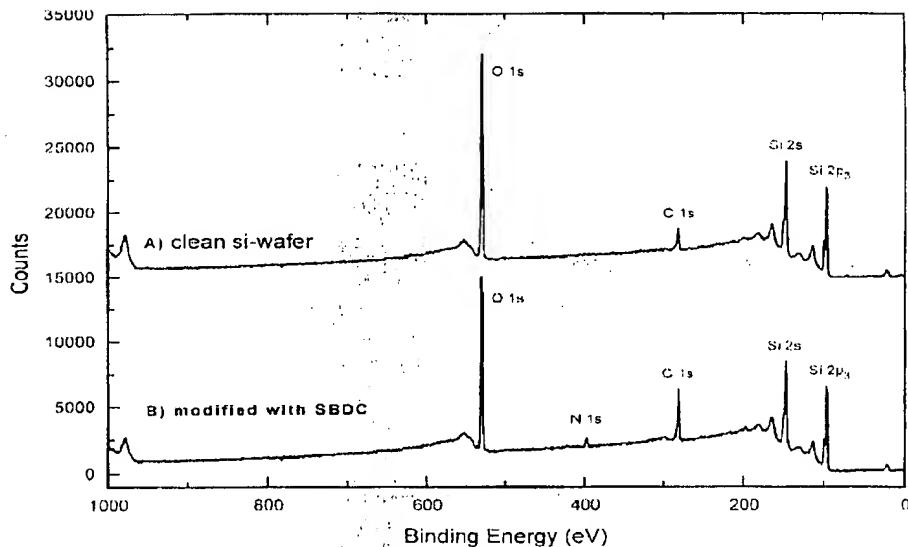


Figure 1. XPS spectra of (A) a cleaned silicon wafer and (B) a silicon wafer with the SBDC monolayer.

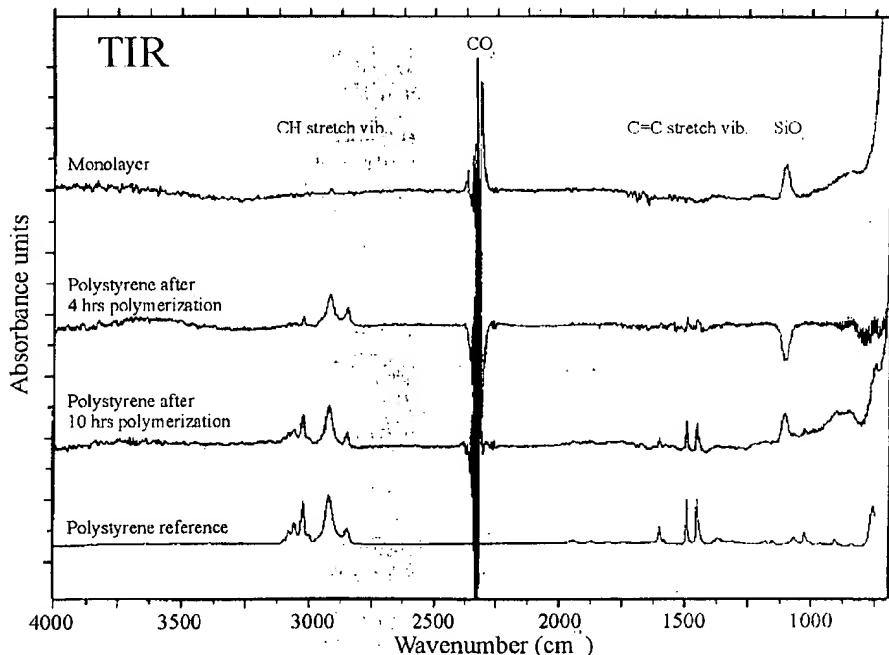


Figure 2. Transmission infrared spectra of Si wafers with SBDC monolayer (top), after photopolymerization of styrene for 4 h (second), after photopolymerization of styrene for 10 h (third), and a polystyrene reference (bottom).

polymerization time is attributed to the growth of polystyrene chains from the surface.

To directly observe these growing layers, extensive SFM studies of the polymer and copolymer layers initiated from the surface-grafted SBDC initiator have been performed. To follow the thickness increase of the growing polymer layer, we employed a patterned glass or silicon wafer surface with chromium lines, made by photolithography. Chromium is not sensitive toward oxidation under these conditions, and the SBDC initiator monolayer is not grafting onto this metal. Only the uncovered silicon surface between the lines is coated with SBDC. This method has been used before by Fujihara et al.²⁹ to prepare controlled regions of fluorinated silane monolayers.

In the present study we used the height differences, measured with SFM, between the chromium and the

substrate for determining directly the polymer layer thickness during photopolymerization. If the initiator SBDC monolayer, deposited between the chromium lines, initiates a "living" free radical polymerization, the layer thickness would increase with polymerization time. After each time step of photopolymerization the samples were sonicated and rinsed thoroughly to ensure that no adhesion of nongrafted polymers would occur. We like to emphasize here that homopolymer, which might be produced due to side reactions,²⁵ will be removed by the vigorous cleaning procedure. In Figure 3, topographic images, cross sections, and the schematic representations of typical growing homopolymer and block copolymer layers for a photopolymerization in various time steps are shown. The chromium lines are 155 ± 0.5 nm high and $0.4 \mu\text{m}$ wide. The space between the lines is $0.6 \mu\text{m}$, ensuring an asymmetry in the

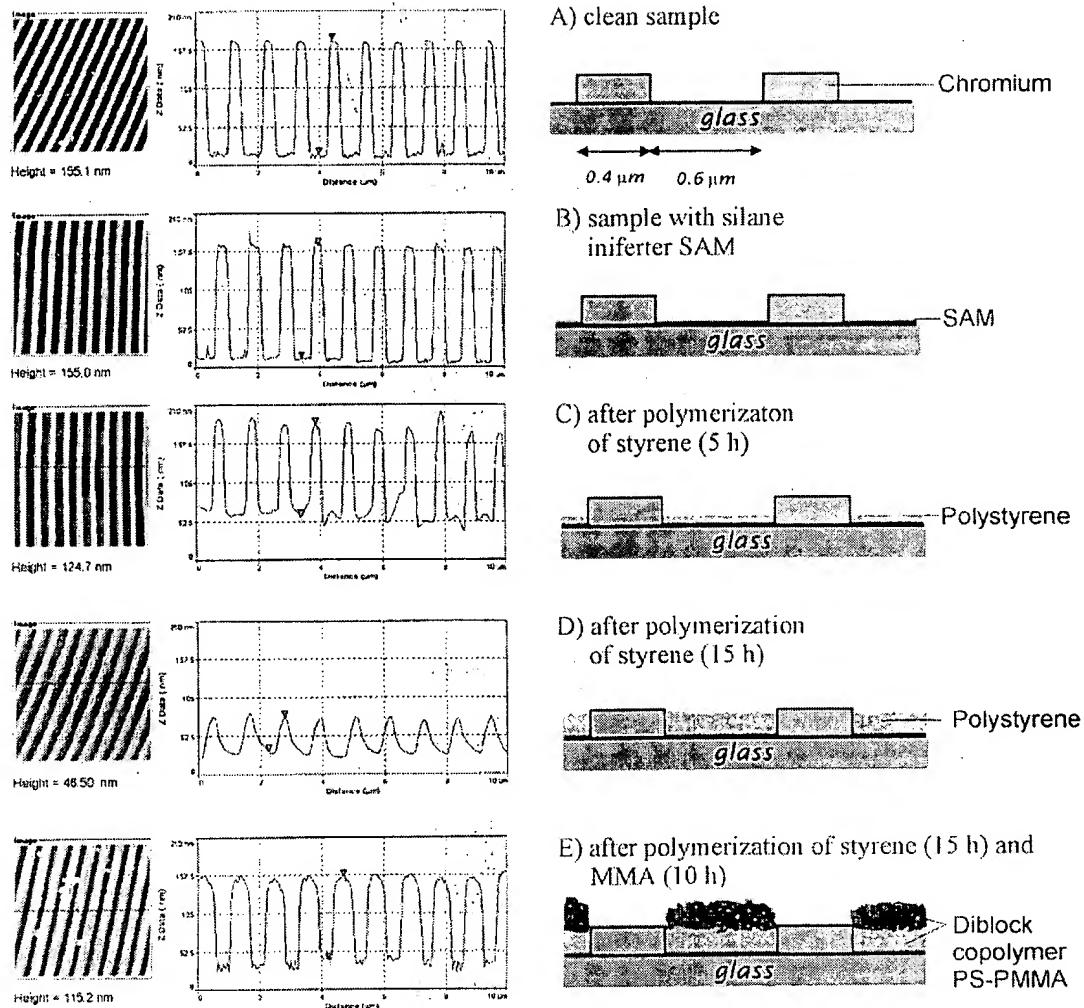


Figure 3. Topographic images, SFM scan lines, and schematic cross-sectional representation of glass slides with chromium patterns and the formation of the polymer and copolymer layer: (A) cleaned sample, (B) sample modified with SBDC, (C) after photopolymerization of styrene for 5 h, (D) after photopolymerization of styrene for 15 h, and (E) after photopolymerization of styrene for 15 h and subsequently MMA for 10 h.

pattern and facilitating the observation of the growing polymer layer. The scanned area is $10 \times 10 \mu\text{m}$. At least three scans at different places were taken for each measurements to confirm the results. The topographic images in Figure 3 depict five different stages in the polymerization process. The first image (Figure 3A) is the clean sample from which the starting height differences were determined. After deposition of the initiator SBDC monolayer (Figure 3B), no change in the height differences was observed. This was expected, since the layer thickness of a SBDC is $\sim 1 \text{ nm}$, which is just beyond the resolution of the SFM in the particular experimental conditions. Moreover, larger changes in the height differences at this stage would point to polysiloxane, formed in solution from the (trimethoxy)silanes, that is adhering to the surface, or to the formation of SBDC multilayers. Obviously, such adverse effects are not present.

After exposing the sample to UV irradiation in a styrene solution for 5 h, the expected change in height difference was observed (Figure 3C). The growing chains fill the gaps between the lines to a height of $25 \pm 5 \text{ nm}$, which is the thickness of the polymer layer that has been formed. When the same sample was used again for subsequent polymerization of styrene for 10 h, the

layer thickness increased to $104 \pm 5 \text{ nm}$ (Figure 3D). Finally, the formation of a diblock copolymer was explored using MMA as the monomer for the second block. The sample, with a polystyrene layer grown for 15 h in total, was exposed to UV irradiation for another 10 h in MMA solution (Figure 3E). This yielded an inverse image: the block copolymer had exceeded the thickness of the chromium lines (155 nm), and the total thickness of the block copolymer layer had become $270 \pm 5 \text{ nm}$. To verify that polymer did not grow or overflow on the chromium strips of the patterned surface, we used the SFM in the tapping mode configuration. Figure 4A displays a clean chromium-lined sample where the glass and chromium surfaces are comparable in hardness. The thin strips at the edges of the lines are due to topographic effects. The image on the right (Figure 4B) shows the relative hardness after monolayer deposition and 15 h of styrene photopolymerization. Here, the contrast between hard (bright) and soft (dark) areas is obvious, indicating the formation of the polystyrene layer only outside the chromium lines. Similar results have been obtained in the block copolymer case.

The continued growth of the polymer layer (Figure 3) when the sample is again irradiated by UV light after an interruption is the first proof of the "living" character

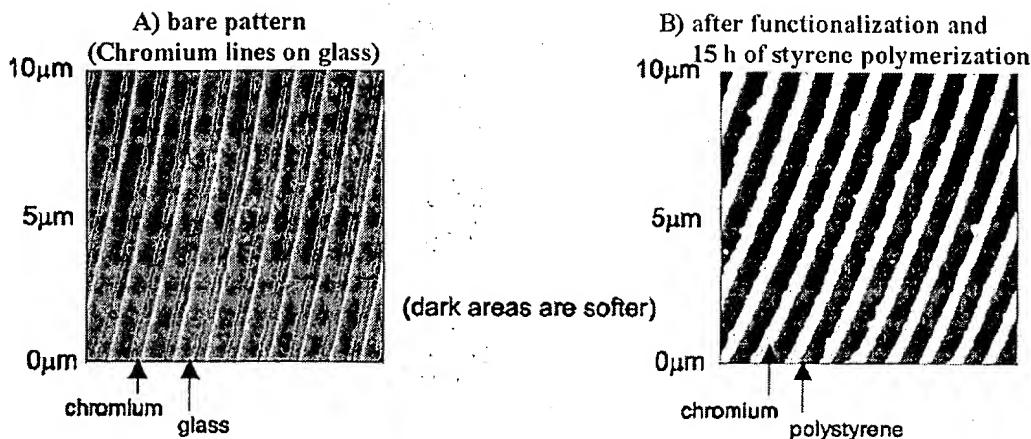


Figure 4. SFM images of the relative hardness of the surface of (A) a clean, chromium-patterned sample and (B) the same sample with grafted SBDC and subsequent photopolymerization of styrene for 15 h.

of the surface-initiated photopolymerization. Further proof of the "living" character of the photopolymerization is the fact that the consecutive use of two different monomers results in the formation of a diblock copolymer layer. According to the literature,²⁵ in the cross-polymerization from PS to PMMA some difficulties might occur regarding the photolysis of dithiocarbamate end groups on the PMMA growing end, resulting in a less efficient "living" character of the block copolymerization. In our experiments, however, we have a "confined two-dimensional photopolymerization" process where, due to the high grafting density, the surface-growing polymer end explores only a two-dimensional space and grows in a uniform way as well as for the first and the second block layer. It is possible that the surface-initiated "living" photopolymerization proceeds in a more efficient way and with fewer side reactions than in solution polymerizations. In fact, if during the polymerization of the first monomer, styrene; homopolymer is produced, its inclusion in the grafted polymer layer would be energetically unfavorable due to the entropy loss, and it will be washed out in the cleaning process. If during the polymerization of the second monomer, methyl methacrylate, block copolymer was not formed, then no further increase in the layer thickness would be observed. Homopolymethacrylate, if formed, would not be compatible with the grafted polystyrene layer due to unfavorable enthalpic and entropic factors. If, however, both grafted block copolymer and homopolymer are formed, the surfactant effect of the grafted block copolymer will be very inefficient. Consequently, the homopolymethacrylate is not dissolved into the grafted block copolymer layer and will be removed in the cleaning process. The observed thickness increase after the polymerization of the second monomer is therefore due to the formation of the block copolymer. Furthermore, if in all cases above homopolymers would have been produced and subsequently removed, this would have resulted in a sublinear increase of the layer thickness. On the contrary, a linear increase in the layer thickness has been observed (Figure 5).

The same methodology as above (measuring layer thicknesses with SFM) was also used to determine the growth of the polymer layer with time. Several samples corresponding to increasing photopolymerization times were measured. The results are shown in Figure 5 and demonstrate a linear relation between the increase of

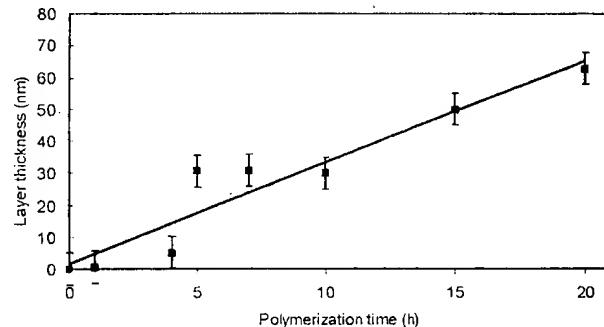


Figure 5. Layer thickness versus photopolymerization time for styrene initiated by grafted SBDC on patterned Si wafers.

the layer thickness, averaged over at least 20 spots per sample, and the polymerization time. The large error bars are due to the fact that the layer thickness is not only determined by the polymer chain length but also by the grafting density of the initiator, a parameter which is difficult to control with accuracy. As a consequence, there is a large variation of the layer thicknesses from sample to sample. The continuous increase, however, in layer thickness, as displayed by the line fitted with linear regression, is the result of linear growth of the polymer chains from the surface, as expected with "living" polymerizations in general.

Viewing a cross section of a sample with a surface-grafted polymer layer by means of electron microscopy will further complement the insights into the characteristics of our polymerization with surface-grafted initiator initiators. For this, a scanning electron microscope (SEM) was used. The monolayer was prepared on a Si wafer, and photopolymerization of MMA for 15 h and subsequently styrene for another 15 h was performed. The wafer was then broken, and the edges of the pieces were investigated with SEM (Figure 6). Here, a polymer layer of about 100 nm thick is clearly visible as the light-gray band in the middle. The dark-gray area on the right is the silicon substrate, while the thin white line at the left edge of the polymer layer is due to scattering of the electron beam. This thickness is in agreement with the results obtained with the SFM measurements. With the use of TEM the formation of block copolymer was unambiguously confirmed. In Figure 7, a TEM image after 15 h of styrene and 15 h of MMA photopolymerization is shown. TEM samples were prepared by using small disks (diameter ca. 0.8

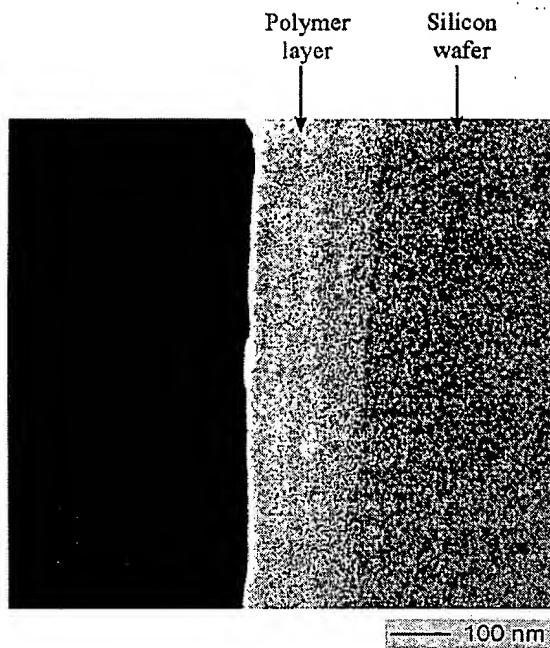


Figure 6. SEM image of PMMA-PS block copolymer grafted on the surface.

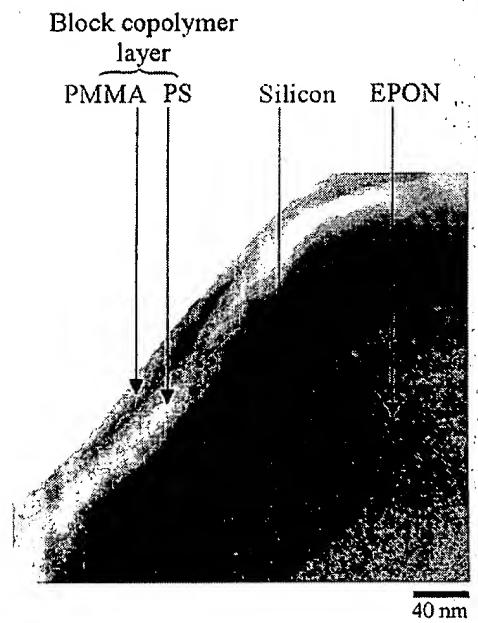


Figure 7. TEM image of block copolymer layer of PS-PMMA grafted on the surface (stained for 19 h with OsO_4).

cm) of a cross-linked epoxy resin (EPON), which were covered with 40 nm of silicon via evaporation with an electron beam. The epoxy resinous substrate used in this method, coated with a thin silicon film, could be treated in the same way as normal Si wafers. At the surface of this layer, the iniferter (SBDC) from which the copolymerization was performed was grafted. After staining with OsO_4 for 19 h, two distinct layers appeared, namely a bright layer (30 nm) covered by a very thin darker layer (15 nm). As OsO_4 stains PMMA more selectively, the upper layer is PMMA, as expected. The fact that the top layer is thin is due mainly to its depolymerization by the electron beam. Thus, direct evidence for the formation of a block copolymer layer on the surface is

obtained. The confirmation of the existence of the block copolymer layer with TEM imaging demonstrates in an elegant way our initial objective of initiating a "living" free radical polymerization from a surface, producing thus, in a controlled manner, grafted thin homopolymer and block copolymer layers.

Conclusions

To modify the surface properties of (in)organic materials, we successfully covalently attached a stable monolayer, with high grafting density, of *N,N*(diethylamino)dithiocarbamoylbenzyl(trimethoxy)silane on the surface of silicon wafers and glass slides, thereby creating a surface-grafted photoinitiator for "living" free radical photopolymerization. In this way, we have been able not only to change the hydrophilicity of the surface by polymerizing different monomers but also to create polymer bilayers, which are directly tethered to the surface. The increase in layer thickness after photopolymerization was directly measured by SFM using silicon wafers patterned with chromium. Furthermore, the samples were characterized by contact angle measurements, XPS, transmission IR, SEM, and TEM. The photopolymerizations of styrene and MMA monomers were used to demonstrate the surface-initiated "living" free radical photopolymerization representing a polymerization method in a "confined two-dimensional space". This is supported by (a) the linear increase of the polymer layer thickness, (b) the reinitiation of the photopolymerization after interruption of the process, (c) the occurrence of block copolymerization after switching from styrene to a methyl methacrylate monomer, and (d) the formation of a well-defined homopolymer monolayer or block copolymer bilayer.

Thus, a "living" free radical polymerization, initiated from a surface-grafted monolayer of an iniferter initiator, has been demonstrated, providing new ways to modify the properties of substrate surfaces and to create polymer monolayers and block copolymer bilayers and opening new routes toward functional surfaces.

Acknowledgment. We thank FOM and the Dutch Science Organization (NWO-CW) for financial support. Furthermore, we thank H. Nijland for the SEM images, F. J. Esselink for TEM images, A. Heeres and J. de Vries for the XPS measurements, and H. C. van der Mei for assistance in the contact angle measurements. Finally, we thank P. F. van Hutten for his comments and suggestions.

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Spatio-Resolved Hyperbranched Graft Polymerized Surfaces by Iniferter-Based Photograft Copolymerization

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Two different types of three-generation hyperbranched graft surfaces with parent chain (stem), daughter chain (branch chain), and granddaughter chain (twig chain) were sequentially prepared by iniferter (initiator-transfer agent-terminator)-based quasi-living radical graft copolymerization using photolysis of the benzyl *N,N*-diethyldithiocarbamate (DC) group. The graft copolymerization of chloromethylstyrene (CMS) with *N,N*-dimethylacrylamide (DMAAm) or *N,N*-dimethylaminoethyl methacrylate (DMAEMA) was initiated on DC-derivatized surfaces under ultraviolet irradiation, followed by dithiocarbamylolation on CMS units in the graft copolymer chains. The repeated cycles of photopolymerization/dithiocarbamylolation provided successively higher generations of graft architectures. The stepwise progress of the branching stage was evidenced with changes in surface elemental composition and wettability and visualized by dye staining. From the typical force-versus-distance curves obtained by atomic force microscope measurement, some structural information of graft polymers was estimated.

Introduction

Precise architecture of surface graft chains may be needed for prevention of biocolloidal adsorption and adhesion in biomedical applications. Conventional radical graft polymerization techniques cannot control molecular parameters such as chain length and chain shape including block and branching due to the high reactivities of free radicals.¹ However, recent progress in the controlled radical reactivity technique at propagating chain ends,^{2–4} including nitroxide-mediated stable free radical polymerization (SFRP),^{2,5–8} atom transfer radical polymerization (ATRP),^{3,9–12} and reversible addition–fragmentation chain transfer polymerization,¹³ has enabled the design of precise

and elegant macromolecular architectures.^{14–20} Highly branched or hyperbranched polymers have drawn the attention of various research groups for 10 years, and a variety of hyperbranched polymers have been prepared.^{21–34} The majority of hyperbranched polymers have been made using step growth polycondensation reactions of AB₂ type monomers, where A and B represent two different functional groups. On the other hand, on surface polymerization few hyperbranched polymer surfaces were prepared.

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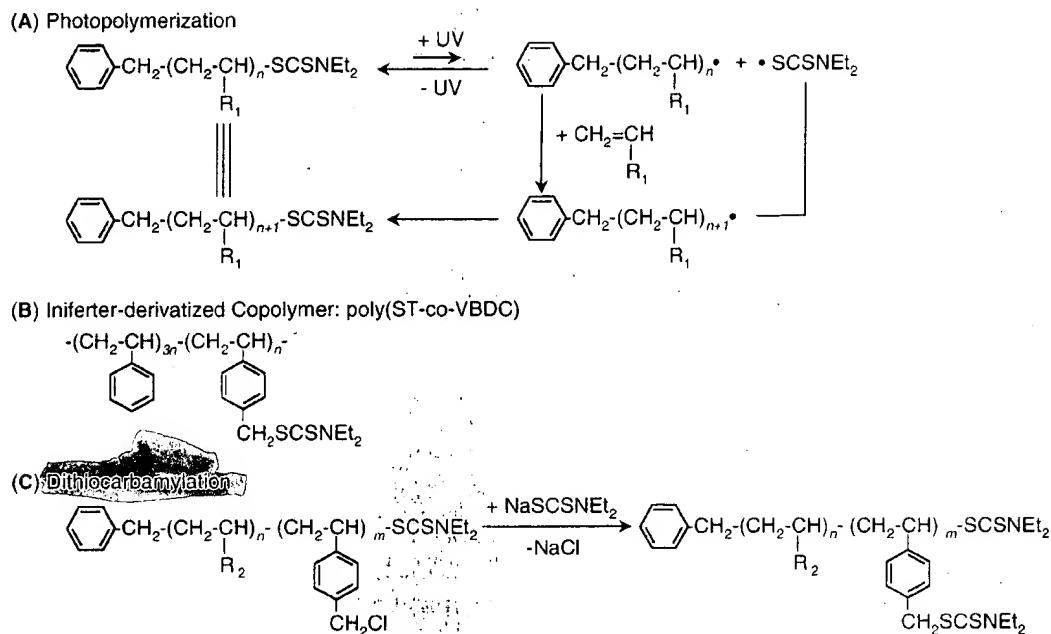


Figure 1. (A) Reaction mechanism of the iniferter-based quasi-living radical polymerization. (B) Chemical structure of dithiocarbamate group derivatized polyST (poly(ST-*co*-VBDC)). (C) Reaction mechanism of dithiocarbamylation of chloromethylstyrene group derivatized polymer.

Our attempt to design a precision surface graft architecture utilized photochemistry of *N,N*-diethylidithiocarbamate (DC) by which reversible transformation between an active and a dormant species at a propagating end is strictly controlled, leading to quasi-living polymerization.^{35–39} This iniferter polymerization method (Figure 1A), which was first developed for controlled macromolecular architecture in solution by Otsu et al.^{40,41} in the early 1980s and proceeds during ultraviolet (UV) irradiation at room temperature, is particularly beneficial to surface functionalization on fabricated biomedical devices. Applying this iniferter-based polymerization method, the authors have designed various surface graft architectures controlling the chain length,³⁵ block graft chain,^{35,36} gradient chain length,^{35,37} and regionally graft-polymerized pattern^{35,37,38} surface.

More complex but controlled hyperbranched graft architectures were prepared in our previous paper.³⁹ The principle is based on a sequential reaction of iniferter copolymerization with chloromethylstyrene (CMS) and subsequent dithiocarbamylation of the CMS units in the copolymers. After a stem (parent) chain was progressively propagated from an iniferter-immobilized surface, CMS units in graft chains were dithiocarbamylated. Subsequently, a branch (daughter) chain was progressively propagated on multiply derivatized iniferter units in the stem chains. The chain length for both parent and daughter chains was controlled by photoirradiation time, and the degree of branching was determined by the composition of CMS units. Figure 2 represents the

schematics of the preparation of the first generation (G1) to n th generation (G n) graft architectures, in which each generation consists of two steps: dithiocarbamylation (Figure 1C) as multiple iniferter-derivatized sites on chains and subsequent iniferter polymerization (Figure 1A). Semiquantitative analysis of the graft chain lengths of stem and branch chains was assessed by the newly developed differential fluorescent technique, which convinced us that a well-controlled graft architecture was realized as designed.

In this study, as an extension of our series of studies on controlled hyperbranched graft surface designs, a three-generation branched-graft architecture consisting of parent (stem), daughter (branch), and granddaughter (twig) chains was prepared. Some insight into structural information on the graft architecture was provided by force-versus-distance curves measured by atomic force microscope (AFM).

Materials and Methods

Materials. CMS (*m*- and *p*-mixture) was obtained from Tokyo Chemical Industry Ltd. (Tokyo, Japan). Styrene (ST) was purchased from Ohken Co., Ltd. (Tokyo, Japan). Solvents and other reagents, all of which were of special reagent grade, were obtained from Wako Pure Chem. Ind. Ltd. (Osaka, Japan) and used after conventional purification. Poly(ethylene terephthalate) (PET) film was obtained from Toray Co., Ltd. (Tokyo, Japan).

DC-Derivatized PolyST Coated Surface. DC-derivatized polyST was prepared according to the method previously reported by us.⁷ Briefly, the mixture of ST (0.83 g, 8.0 mmol) and vinylbenzyl *N,N*-diethylidithiocarbamate (VBDC, *m*- and *p*-mixture, 0.53 g, 2.0 mmol) in *N,N*-dimethylformamide (13.7 mL) including AIBN ([monomer]/[initiator] = 100, molar ratio) was shaken for 3 h at 60 °C. The resulting poly(ST-*co*-VBDC) copolymer (DC-derivatized polyST) was purified by reprecipitation in a toluene–methanol system three times. The yield was 0.12 g (8.5%). The molecular weight of the polymer was estimated by gel permeation chromatography (GPC) analysis: $M_n = 51\,400$ (PST standard, eluent CHCl_3). The content of DC unit in the copolymer, which was determined by ¹H NMR spectroscopy from the integral ratios between the aromatic protons (δ 6.3–7.2) and the remaining S-methylene protons (δ 4.2–4.6) of the dithiocarbamate group.

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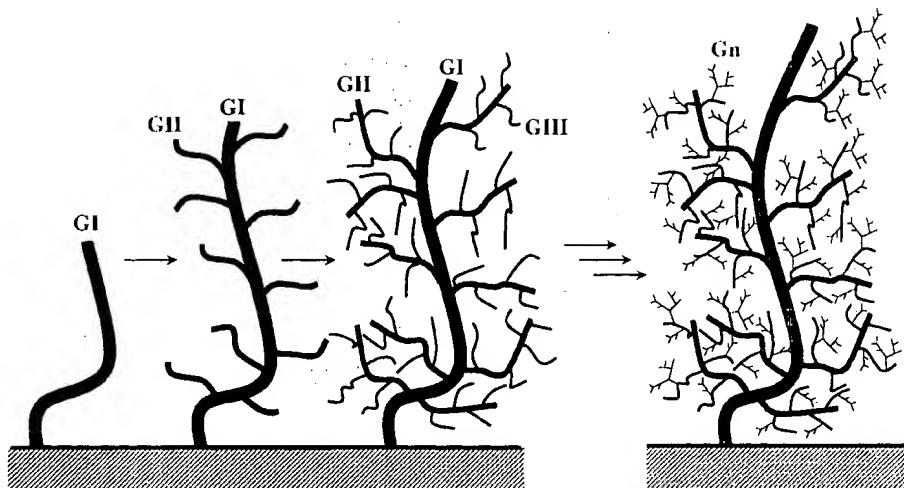


Figure 2. Schematic drawing of the first generation (G1) to *n*th generation (G_n) graft architectures.

carbamyl group, was found to be 25.1 mol %. A toluene solution of the DC-derivatized polyST (3 mL, 1%) was coated on PET films (15 × 15 mm), which were used as substrates.

Surface Photograft Polymerization. The DC-derivatized polyST films were placed in a glass dish (diameter 30 mm), poured with 0.5 mL of a monomer-containing methanol solution (0.5 mol/dm³), and then covered with a sapphire plate (diameter 25 mm, thickness 1 mm). Monomers used were CMS, *N,N*-dimethylacrylamide (DMAAm), and *N,N*-dimethylaminoethyl methacrylate (DMAEMA). The films were then UV-irradiated through the sapphire plate in an atmosphere of nitrogen with an ultrahigh-pressure mercury-vapor lamp (250 W, SPOT CURE250, Ushio Inc., Tokyo, Japan). The light intensity, measured with a photometer (UTR-1, Topcon, Tokyo, Japan), was 5 mW/cm². The temperature of the polymerized samples was maintained around 20–25 °C. The photograft-copolymerized films were rinsed with methanol and ethanol and then dried in air.

Preparation of Multiple-DC-Derivatized Film. The poly(CMS-*co*-DMAAm) or poly(CMS-*co*-DMAEMA) graft-copolymerized films were immersed in 10 mL of an ethanol solution of sodium *N,N*-diethyldithiocarbamate trihydrate (2 g, 9 mmol). After the solution was shaken for 24 h at room temperature, the multiple-DC-derivatized film was obtained. The films were thoroughly rinsed with ethanol, dried in air, and stored in a dark desiccator.

Preparation of Regionally Different Graft-Copolymerized Surface. DC-derivatized polyST film was tightly placed on a photomask with a linear opening (line width 2, 1, or 0.5 mm) (Four Leaves Co., Ltd., Osaka, Japan) and covered with a sapphire plate after being filled with a monomer-containing methanol solution. The films were irradiated through the photomask, rinsed with water and alcohol, and then dried in air. After immersion into an ethanol solution of methyl iodide, the surface-grafted films were stained with a dilute aqueous solution of rose bengal (Acid Red 94, C.I. 45440) (1.0% w/v) for visualization of the graft-copolymerized region.

Physical Measurements. All ¹H NMR spectra were recorded in CDCl₃ solution using tetramethylsilane (0 ppm) as an internal standard with a 270 MHz NMR spectrometer (GX-270, JEOL, Tokyo, Japan) at 30 °C. X-ray photoelectron spectra were taken with a Shimadzu ESCA 3400 (Kyoto, Japan) using a magnesium anode (Mg K α radiation) at room temperature and 3 × 10⁻⁶ Torr (10 kV, 20 mA). Static contact angles toward deionized water were measured with a contact angle meter (Kyowa Kaimen Kagaku Co., Ltd., Tokyo, Japan) at 25 °C by the sessile drop method. Force-versus-distance curves were obtained by AFM (Dimension 3000, Digital Instruments, Santa Barbara, CA) using a probe tip with spring constant (0.12 N/m) and operated at the frequency of the approach/retract cycle of 3.2 Hz. AFM images (400 × 400 pixels) were obtained using the "height mode", which kept the force constant, and visualized using the "surface mode".

Cross-sectional topography of selected regions in the AFM images was obtained with Digital Instruments software.

Results

Two different types of three-generation-graft chains were prepared from the iniferter-based copolymerization of CMS with DMAAm or DMAEMA on surfaces thinly coated with the iniferter-derivatized copolymer (poly(ST-*co*-VBDC); content of DC unit, 25 mol %) (Figure 1B). The grafted chains of DMAAm exhibited a water-soluble, nonionic character in water, whereas those of DMAEMA further subjected to quaternization exhibited a water-soluble, cationic character.

Preparation of Nonionic Hyperbranched Grafts: Stem–Branch–Twig Architecture. Iniferter-driven surface photograft copolymerization was initiated from the surface of the DC-derivatized polyST film (generation 0, G0 in Figure 3) in methanol solution containing CMS and DMAAm at a feed mole ratio of 1:20 (step I in Figure 3). After 5 min of irradiation, the treated surface was immersed into ethanol solution containing sodium *N,N*-diethyldithiocarbamate for 24 h (step II in Figure 3). X-ray photoelectron spectroscopy (XPS) measurement showed both markedly increased C/C and N/C ratios upon photoradiation, and markedly reduced C/C and increased S/C were observed upon dithiocarbamylation (Figure 3A). These indicate that CMS–DMAAm graft-copolymerized chains as the stem chains were produced on the treated surface (stem architecture: first generation (G1), b in Figure 3) and then on multiple-DC-derivatized CMS units (c in Figure 3). In a separate solution experiment using benzyl *N,N*-diethyldithiocarbamate as a soluble iniferter, the composition of copolymer, produced under the same conditions as the surface graft copolymerization mentioned above, was found to be approximately 20 mol % for polyCMS (data not shown). This suggests that the graft chain was composed of one CMS unit per five monomer units on an average.

The successive sequential procedure of photopolymerization (step III in Figure 3) and dithiocarbamylation (step IV) under the same conditions employed for the stem architecture resulted in the same trend for the changes in C/C and S/C ratios (Figure 3A). These indicate that branched graft chains were produced (branch architecture: second generation (GII), d in Figure 3) followed by multiple-DC-derivatized CMS units (e in Figure 3).

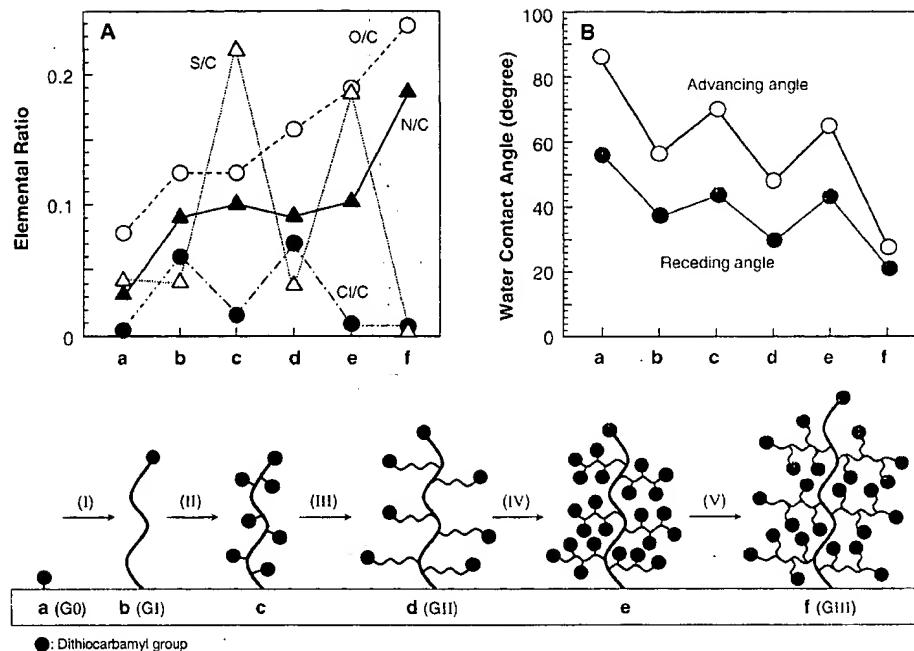


Figure 3. (A) Elemental ratio in XPS measurements and (B) water contact angle changes in the sequential progress of the branching stage by the alternate reactions of photograft copolymerization and dithiocarbamylation from the nongrafted DC-derivatized surface (G0) to the third-generation surface (GIII) and schematic drawing of the stage progress.

Photoirradiation on such treated film in DMAAm aqueous solution (step V) resulted in markedly increased O/C and N/C ratios close to the theoretical value (0.20) whereas little significant detection of Cl and S atoms was observed, indicating that polyDMAAm was grafted on branched chains (twig architecture: third generation (GIII), f in Figure 3).

Figure 3A,B summarizes the changes in relative elemental intensity to carbon atom and water contact angle as a function of a repeated series of photopolymerization and dithiocarbamylation. The water contact angles, both advancing and receding angle, synchronously decreased upon photopolymerization probably due to the hydrophilic PDMAAm unit but increased upon dithiocarbamylation due to the hydrophobic component of the DC unit.

Regionally Different Third-Generation-Graft Architectured Surface. The DC-derivatized surface with regionally different hypergeneration-graft architectures (the coated surface as previously mentioned) was sequentially prepared from CMS and cationic monomer, DMAEMA, using photomasks with different line widths (2, 1, and 0.5 mm). The conditions of polymerization and dithiocarbamylation were the same as those for PDMAAm hyperbranched grafts mentioned above. After photopolymerization through a photomask tightly placed on the surface, quaternization of the DMAEMA unit was carried out with methyl iodide. These sequential reactions using different-sized photomasks were repeated three times. First, the stem architecture surface was prepared in a 2 mm striped pattern (G1) on the DC-derivatized surface (G0). Second, the GII surface was created with a 1 mm striped pattern on the G1 grafted region, and last, the GIII surface was created with a 0.5 mm striped pattern on the GII grafted region. Rose bengal (anionic dye) staining after quaternization clearly differentiated the sequential formation of the regionally different multi-generation-graft architectures as shown in Figure 4. It was apparent that the qualitative color intensity of stained areas was in the order of GIII > GII > G1 > G0 (nontreated).

Force-versus-Distance Curve with the AFM. To characterize the nature and structure in water of the prepared regionally different multigeneration-graft architecture shown in Figure 4, force-versus-distance ($f-d$) curves using an atomic force microscope were determined in water between the grafted layer and the AFM silicone nitride probe tip. There was a marked difference in the $f-d$ curves between nongrafted and grafted surfaces (Figure 5). When the tip was lowered to contact with the nongrafted (G0) surface, the repulsive force was generated as a linear function of tip distance (note that this is due to the enforced bending of a cantilever upon pushing down to the surface; theoretically, a very sharp repulsion force should be observed for nondeformable surfaces if the cantilever does not bend upon high loading) (Figure 5A). There was no appreciable hysteresis between approaching and retracting traces, indicating that there was little appreciable detachment force usually observed for the $f-d$ curve of the retracting trace on hydrophobic surfaces.

On the other hand, for the G1 surface, a slightly exponential $f-d$ curve was found for the approaching trace and hysteresis between the approaching and retracting traces was observed, indicating the formation of graft-polymerized layer (Figure 5B-1). The graft density was estimated to one chain per $20-30 \text{ nm}^2$ ($\sim 0.04 \text{ chain/nm}^2$) from our recent AFM study.⁴² When the cantilever tip was sufficiently pushed down on the surface, the $f-d$ curves for both traces became identical. The separation point of the $f-d$ curves of these traces was conveniently defined as the completely compressed state generated by enforced loading. The repulsive interaction distance between the completely compressed location (position a in Figure 5B-1, top of the compressed graft layer) and the repulsion-initiating location (position b in Figure 5B-1, top of the swollen graft layer) where repulsive force is first appreciated in an approaching trace was roughly estimated as about 100 nm. In a water-swollen graft layer,

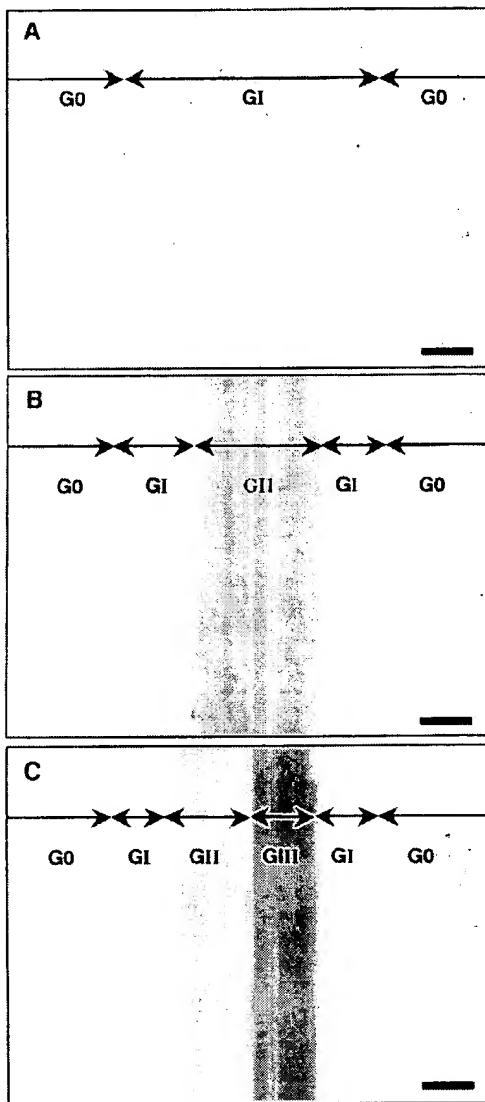


Figure 4. Visualization of the sequential progress of the branching stage by staining with rose bengal. The DC-derivatized polyST surface (G0) was graft-copolymerized with CMS and DMAEMA, followed by quaternization, while narrowing the irradiation area in each polymerization stage (A, GI; B, GI + GII; C, GI + GII + GIII) by the combination of three kinds of photomasks with linear openings (line width: 2 mm for GI, 1 mm for GII, 0.5 mm for GIII). Bar = 0.5 mm.

the real thickness of a graft layer can be defined as the sum of the compressed graft thickness and the repulsive interaction distance.⁴³ The compressed thickness, determined by cross-sectional analysis from AFM scanning images of the boundary area between the grafted and nongrafted regions in air, was about 30 nm (Figure 5B-2). Therefore, the real thickness was estimated as about 130 nm in the GI surface. The observed hysteresis and appreciable detachment strength in the $f-d$ curve, estimated from an adhesive jump in the retracting trace and multiple jumps, strongly suggest that the tip/graft layer interaction was complex.

The GIII surface had a much higher compression force, larger repulsion interaction force, and higher degree of

hysteresis than the GI surface, indicating that although cationically charged water-soluble polyDMAEMA graft chains show steric interaction as the tip approaches the outermost layer of the graft chain in water, once the tip is forced to penetrate into a graft layer, high resistance to deformation and high detachment force are exhibited (Figure 5C-1). The real grafting thickness of the GIII surface was about 160 nm (the repulsive interaction distance, about 120 nm; the compressed thickness, 40 nm; Figure 5C-2), which was close to the value observed in the GI surface.

Discussion

The repeated cycle of iniferter-based photopolymerization and subsequent dithiocarbamylation produced a controlled graft architecture: the former reaction determines both chain length and content of precursor unit (or branching site), and the latter reaction produces iniferter on derivatization chains. Our previous study preparing a controlled graft architecture of stem and branch chains showed that chain length and degree of branching were semilinearly proportional to photoirradiation time and CMS content in the copolymers, respectively.¹¹ These were quantitatively determined by differential fluorescent intensity between grafted and nongrafted regions using a confocal laser scanning microscope.

This study was extended to design a more complex structure including twig (or granddaughter) chains. XPS measurement and water contact angle measurement clearly showed synchronous changes in elemental ratios and wettability, responding to photopolymerization (chain extension or branching) and dithiocarbamylation (or multiple-derivatized iniferter on a chain) (Figure 3). These results showed that such sequential reactions lead to a more hyperbranched graft architecture. Repeated cycles of photopolymerization/dithiocarbamylation progressively produced higher wettability as the generations of graft architecture progressed. In addition, higher generation graft surfaces were more densely stained, as clearly visualized on the regional multigeneration-graft architecture surface (Figure 4).

On the other hand, structural information on the graft chains in water was obtained by $f-d$ curve using the AFM (Figure 5). In principle, $f-d$ curve measurement could provide invaluable dynamic information on the structure of the swollen graft architecture upon enforced pushing-in of a tip into and pull-out from the swollen graft layer. It was apparent that as multigeneration progressed, hyperbranching of the graft architecture was enhanced, resulting in higher spacio-density of the graft chain. This may reflect the mechanical properties of swollen graft architected surfaces. As evidenced by the comparison of $f-d$ curves of GI and GIII surfaces, with increasing generations a higher steric repulsion was observed as the probe tip made contact with the outermost graft chain and penetrated into a graft layer, both of which were derived from higher spacio-density of graft chains and configuration or topology of hyperbranching. The degree of hysteresis between approaching and retracting traces, which may be derived from the elastic pushing-out force generated upon compression of graft chains, was larger for the GIII surface than for the GI surface. In addition, detachment (or adhesive) strength was found to be larger for the GIII surface than for the GI surface. Multiple adhesion jumps were also observed. These may indicate that higher generation graft chains combine their interactions with the tip when subjected to enforced mechanical loading, resulting in the high elastic modulus of the water-swollen graft layer and a higher probability of multiple

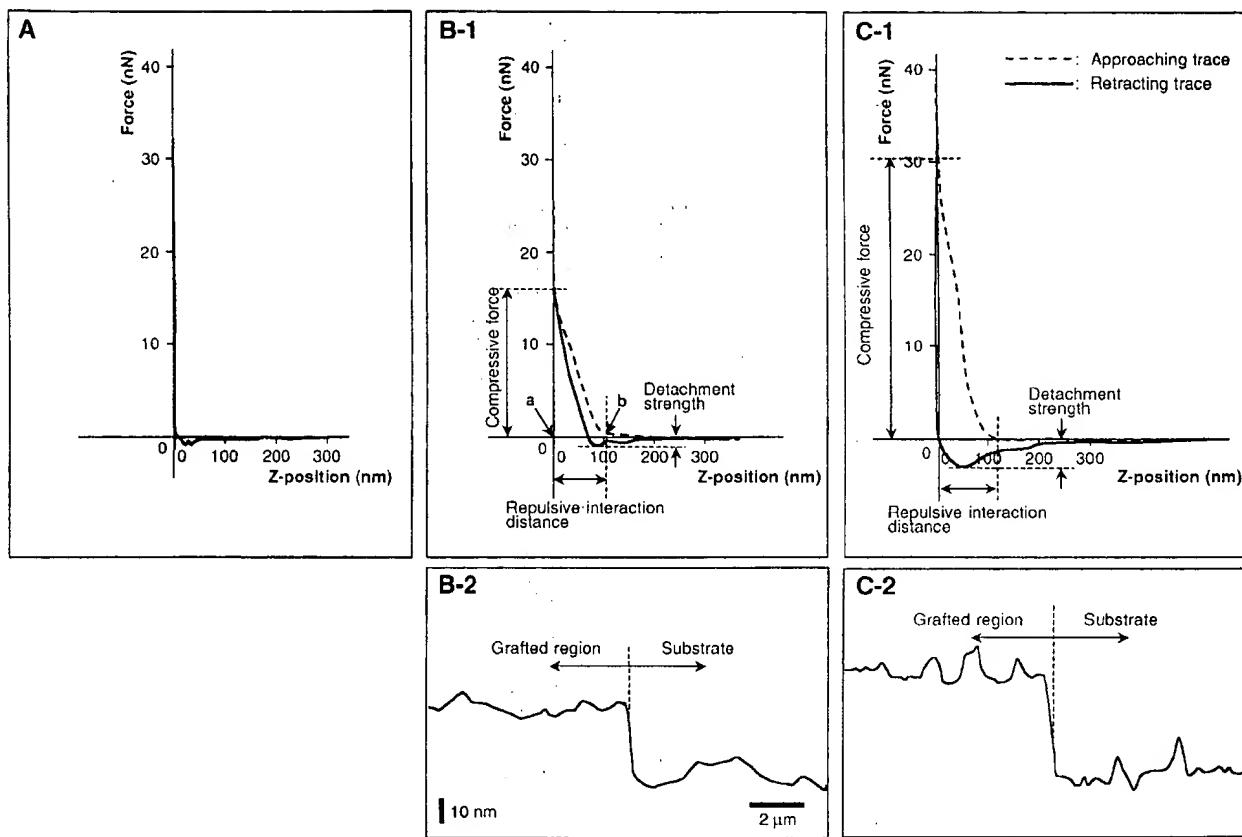


Figure 5. Force-versus-distance (*f-d*) curves using the atomic force microscope on (A) the DC-derivatized polyST surface and CMS-DMAEMA graft-copolymerized surfaces (B-1, GI surface; C-1, GIII surface in Figure 4). Also shown are line scan spectra for the cross-sectional topography between the boundary area of the grafted and nongrafted regions of the GI (B-2) and GIII (C-2) surfaces.

interaction of graft segments with the tip. On the other hand, between the GI and GIII surfaces there was little change in the graft thickness in water, which was defined as the sum of the repulsive interaction distances and the compressed graft thickness, as indicated in our AFM study⁴³ of the water-swellable graft layer. This suggests that the thickness of the graft layer did not significantly increase but the three-dimensional density of the graft chains was elevated with the progress of the graft polymerization stage.

We demonstrated a multigeneration hyperbranched graft architecture up to three generations. However, in principle, higher generation (*n*th) graft architecture is feasible upon repeated cycles of the two reactions described above (Figure 2). The spacio-resolved graft architectural method described here offers multiple choices of graft architectures in terms of main chain length, branch-

branch length, chain composition, and degree of hyperbranching. In addition to the increased spacio-density of graft chains, the configuration or topology of hyperbranching may lead to different mechanical properties as compared with linear grafted chains obtained by conventional radical polymerization methods.

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Living Radical Polymerization in Homogeneous System by Using Initiator: Design of Block Copolymers

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ABSTRACT

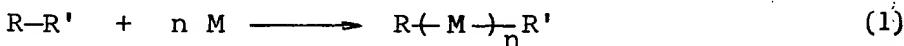
Benzyl N-ethyldithiocarbamate(BEDC) and xylylene bis(N-ethyl-dithiocarbamate)(XEDC) were prepared, and used as mono- and bi-functional photoinitiaters, respectively, of the polymerization of styrene and methyl methacrylate. These photopolymerizations were performed via a living radical polymerization mechanism in homogeneous system. The polymers obtained by BEDC and XEDC still contained one and two reactive N-ethyldithiocarbamate end groups, respectively, bonded at their chain ends. When these polymers were reacted with nucleophiles and copper(II) ion, the chain extension reactions were observed to occur depending on their functionality. By using the polymers obtained by BEDC and XEDC as mono- and bi-functional polymeric photoinitiaters, the AB and ABA block copolymers were also obtained, respectively. Similar results were obtained by using benzyl N,N-diethyldithiocarbamate(BDC) and xylylene bis(N,N-diethyldithiocarbamate)(XEDC) as mono- and bifunctional photoinitiaters, respectively. These results were also compared and discussed.

INTRODUCTION

Since the termination in bulk polymerization of styrene(St) with azobisisobutyronitrile at temperatures below 80°C [1] occurs by recombination, the polymer obtained has two initiator fragments

bonded at its chain ends. However, in radical polymerization of many monomers, the termination by disproportionation and the chain transfer reactions to the compounds existed in the system occur importantly, and hence the number of the initiator fragment per one polymer molecule is always less than 2.

If the initiator ($R-R'$) used has high chain transfer to the initiator and/or primary radical termination reactivities, the polymer with two initiator fragments can be obtained [eq.(1)].

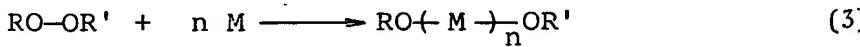
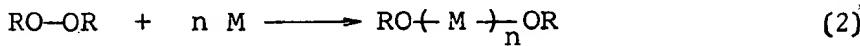


In such cases, the polymer formation is defined as insertion reaction of the monomer molecules (M) into the $R-R'$ bond of the initiator. In a previous paper[2], we proposed to call such initiators initiator-transfer agent-terminator(iniferter). The concept of initiator-transfer agent(inifer) in cationic polymerization has already been proposed by Kennedy[3].

From the above definition, the iniferters can be classified into various types, such as monofunctional iniferter, bifunctional iniferter; thermal iniferter, photoiniferter; monomeric iniferter and polymeric iniferter, etc.

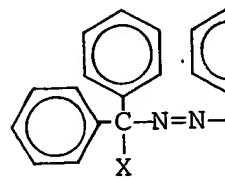
Many initiators which have been used seem to be able to serve as iniferters, if monomers and polymerization conditions are selected. Some examples which may give mono- and bifunctional oligomers or polymers are shown as follows:

a) Peroxides — These compounds show relatively high chain transfer reactivities[1].

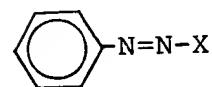
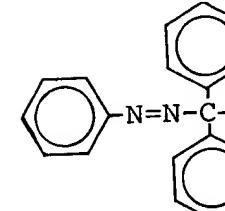


Where R and R' are hydrogen, alkyl and acyl groups.

b) Azo compounds — Aliphatic azo compounds show no chain transfer reactivity (1), but in some tetraphenyl and unsymmetric azo compounds, primary radical termination has been known to occur importantly[4,5].



Where X is :



Where X is :

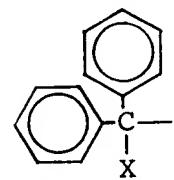
c) Organic sulfur transfer reagents may undergo chain transfer are not so

RS

RS

Where R are

d) Tetraphenylmethylsulfide associate in phenylmethylsulfide they can undergo phenylmethylsulfide termination



Where X is :

Polymerization of
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transfer system occur
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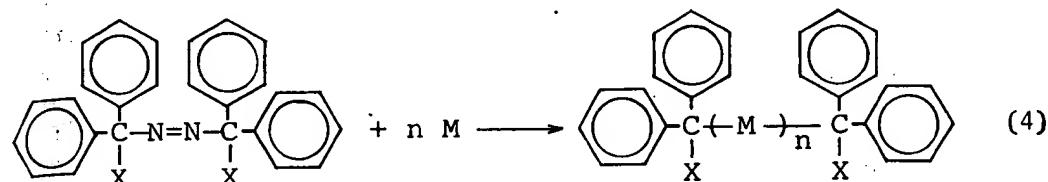
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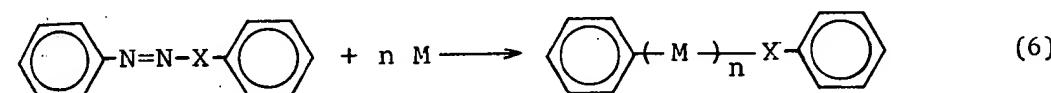
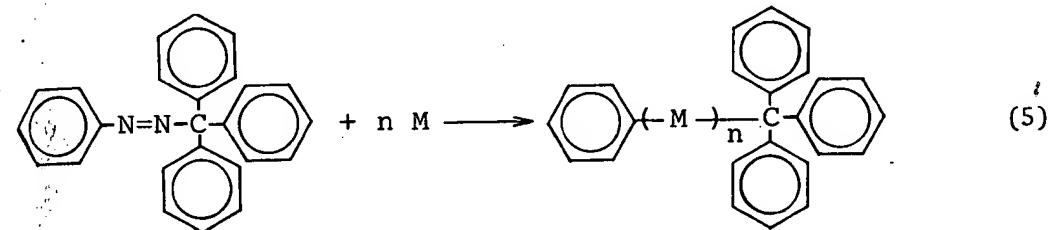
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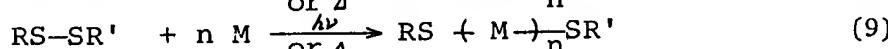
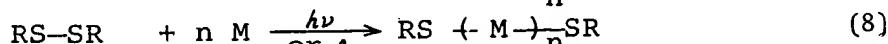
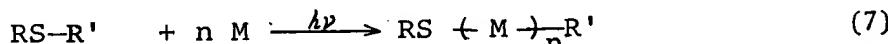


Where X is alkyl and other groups.



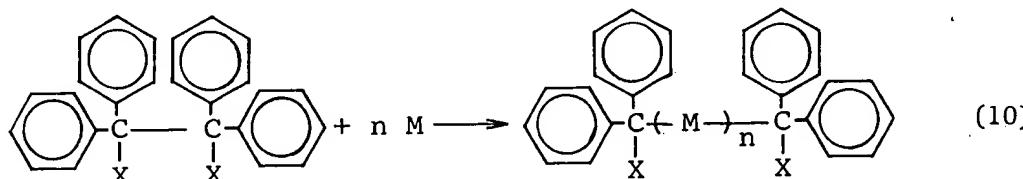
Where X is S and NH groups.

c) Organic sulfur compounds — These compounds show high chain transfer reactivity[6-12] and a part of thiyl radicals produced may undergo primary radical termination[9], because they are not so reactive for initiation.



Where R and R' are hydrogen, alkyl, acyl and thiocarbonyl groups.

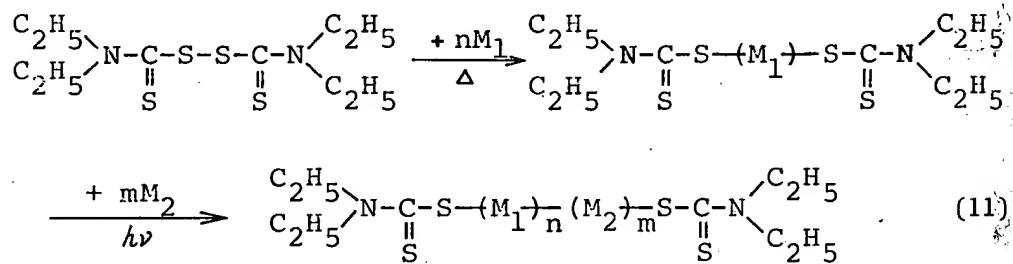
d) Tetraphenylethane derivatives — Hexaphenylethanes easily dissociate into triphenylmethyl radicals which are so stable and they can not enter into initiation[13]. However, some diphenylmethyl radicals can participate into both initiation and termination.



Where X is CN[14], C2H5[15], OC6H5 groups[16].

Thus, when such initiators were used for radical polymerization of vinyl monomers, various mono- and bifunctional oligomers or polymers might be obtained, and used for synthesizing of the other functional and block polymers.

In 1957, we reported that the polymers obtained by tetraethylthiuram disulfide could induce radical polymerization of second monomers leading to block copolymers[17,18], as follows.



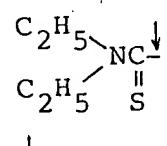
Although this reaction scheme was not ascertained, some block copolymers as polystyrene-*b*-polymethyl methacrylate[17], polystyrene-*b*-polyvinyl acetate[18] and polystyrene-*b*-polyvinyl alcohol[18] were prepared by this technique. Recently, the end group in this polymer was confirmed to be diethyldithiocarbamate sensitive for photo-dissociation, and the number of this end group per one polymer molecule was found to be kept constant as nearly 2 during the polymerization[19]. If these were true, the photopolymerization of vinyl monomers with tetraethylthiuram disulfide is expected to proceed via a living radical mechanism[20] even in homogeneous system which is similar to living ionic polymerization which was discovered in 1956 by Szwarc[21,22].

From such results and consideration, we recently proposed a model for living radical polymerization in homogeneous system by using phenylazotriphenylmethane and tetraethylthiuram disulfide as thermal and photoinitiaters, respectively[20]. This idea is attributed to that a short-lived unstable radical including propagating radical is only existed as its dimer consisting of covalent bond, and if this bond can dissociate, the unstable radical may be supplied into the system. Therefore, this model can be expressed as follows:

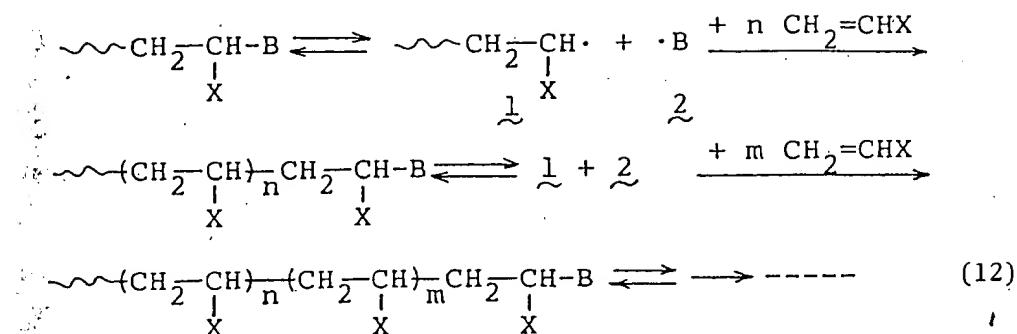
Namely, the thermally or photochemically small radical of the polymer chain, these dissociate in repeated, such living radical phenylmethane aninferters are

Therefore crylate with t weight of the polymerization component bloc merizations pr system, as sho

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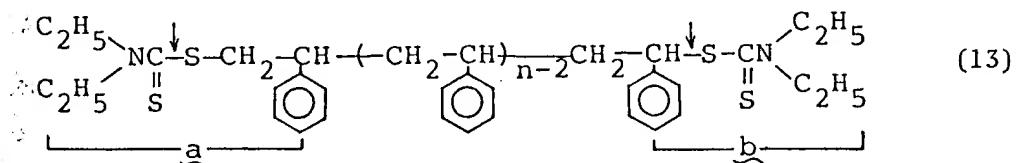
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Namely, the propagating chain ends which can dissociate thermally or photochemically into a propagating radical(1) and a small radical(2) which must be stable enough not to initiate new polymer chain, and recombine easily with propagating radical. If these dissociation, monomer addition and recombination cycles are repeated, such a radical polymerization proceeds apparently via a living radical mechanism. The polymerizations by phenylazotri-phenylmethane and tetraethylthiuram disulfide as thermal and photo-initiators are clear to be an example for such polymerization.

Therefore, in the polymerization of styrene and methyl methacrylate with these iniferters, the yield and average molecular weight of the polymers were found to increase as a function of the polymerization time[20]. The efficient formation of two or multi component block copolymers [23,24] might support that these polymerizations proceeded via living radical mechanism in homogeneous system, as shown in eq.(12).

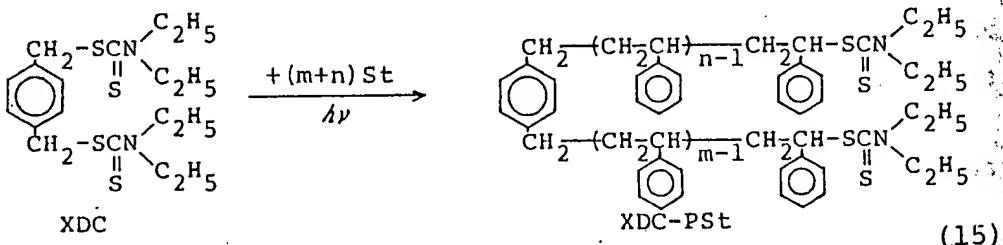
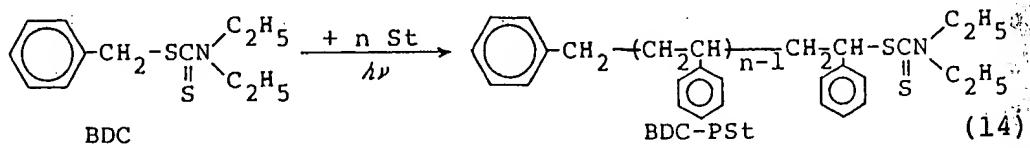
However, the structure of the polystyrene obtained by tetraethylthiuram disulfide, as an example, is expressed by eq. (13) [19].



From this equation, the diethyldithiocarbamate groups are bonded to both polymer chain ends with a different linkage, a and b, which are expected to show different reactivities for photodissociation and initiation. In fact, phenylethyl diethyldithiocarbamate and

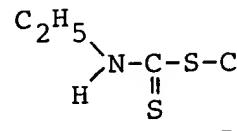
benzyl diethyldithiocarbamate, model compounds for a and b end groups, respectively, were observed to show a different reactivity for initiation as the result of photodissociation at the different C-S bonds[25] which are shown by an arrow in eq.(13), i.e. the latter model compound was effective photoiniferter rather than the former[24].

To design the AB and ABA type structure of block copolymers by this technique, therefore, we must choose mono- and bifunctional polymeric photoiniferters, respectively, which consisted of identical bonds. For this purpose, benzyl N,N-diethyldithiocarbamate (BDC) and xylylene bis(N,N-diethyldithiocarbamate)(XDC) were synthesized, and used as mono- and bifunctional photoiniferters, respectively, in the polymerization of styrene and methyl methacrylate[26]. If these styrene polymerizations proceed according to a living radical mechanism [eq.(12)], the polymers with an identical chain end group seems to always be formed during the polymerization, as is shown in eqs.(14) and (15).



These possibilities were confirmed, and AB and ABA block copolymers were obtained by using polymers obtained by BDC and XDC(BDC-PSt and XDC-PSt), respectively[26]. The results will describe in this paper.

To clarify further these points, benzyl N-ethyldithiocarbamate (BEDC) and xylylene bis(N-ethyldithiocarbamate)(XEDC) were also prepared, and used as photoiniferter of the polymerization of styrene (St) and methyl methacrylate(MMA).



Moreover, XEDC-PMMA), were extension react merization of s copolymers. Th

BDC and XEDC was prepared ethyldithiocarbamate. Crude BDC was silicagel (Wakog colorless viscous NMR spectra (Fig. of p-xylene dicarboxylic acid in benzene/methanol from chloroform confirmed to be pure. Obsd. C 48.5%

Monomers, purifications.

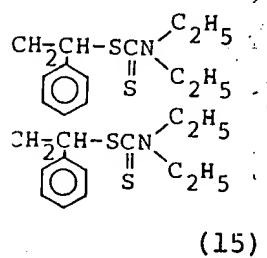
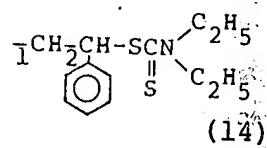
Polymerization in glass tube at a distance of 10 cm from the center of the tube. The polymer weight of the polymer was determined by the weight of the polymer.

Similar polymerization separation of the polymer and block copolymer.

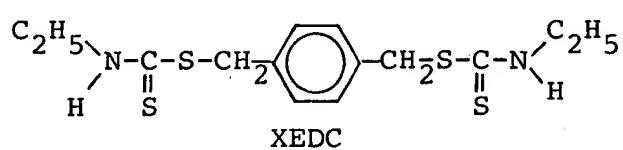
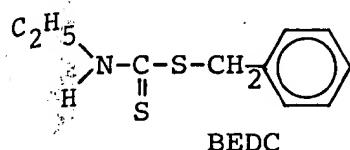
a and b end groups, reactivity for the different C-S i.e. the latter than the

block copolymers and bifunctional consisted of identi-thiocarbamate

[XDC] were synthesized, respectively, methacrylate[26]. to a living identical chain polymerization, as is



block copolymers XDC(BDC-PSt and be in this paper. dithiocarbamate) were also preparation of styrene



Moreover, the polymers, (BEDC-PSt or BEDC-PMMA and XEDC-PSt or XEDC-PMMA), were used as telechelic(end-reactive) polymers for chain extension reaction, and as polymeric photoiniferters of the polymerization of second monomers in order to obtain AB and ABA block copolymers. The results will also shown in this paper.

EXPERIMENTAL

BDC and XDC were prepared according to the previous paper[26]. BEDC was prepared by the reaction of benzyl chloride with sodium N-ethyldithiocarbamate dihydrate in ethanol at room temperature. The crude BEDC was then purified by using column chromatography [column: silicagel(Wakogel C-200), solvent: benzene : n-hexane= 3 : 7]. The colorless viscous liquid thus obtained was confirmed by TLC, IR and NMR spectra(Fig. 1) to be pure. XEDC was prepared by the reaction of p-xylene dichloride with sodium N-diethyldithiocarbamate anhydride in benzene/methanol (1 : 1) mixed solvent at 0°C, and recrystallized from chloroform/n-hexane mixture. XEDC thus obtained was also confirmed to be pure by TLC, IR, NMR(Fig. 1) and elementary analysis:

Obsd. C 48.50, H 5.94, N 8.06%; Calcd. C 48.79, H 5.86, H 8.13%

Monomers, solvents and other reagents were used after ordinary purifications.

Polymerizations of St and MMA were carried out in a sealed glass tube at 30°C under irradiation of Toshiba SHL-100 UV lamp from a distance of 10cm. After polymerization for a given time, the content of the tube was poured into a large amount of methanol to isolate the polymer. The yield of the polymers was determined from the weight of the dried polymers obtained.

Similar procedure was used for block copolymerizations. The separation of the whole polymers into two homopolymers, PSt and PMMA, and block copolymer was carried out by extracting them with cyclo-

hexane/benzene (9 : 1- 7 : 3 vol%), acetonitrile and benzene, respectively. The fractions thus separated were checked by IR spectra.

The intrinsic viscosities, $[\eta]$, were determined viscometrically in benzene at 30°C, and the average-molecular weight (\bar{M}) was calculated by the following equations:

$$\text{For PSt [27]: } [\eta] = 8.5 \cdot 10^{-5} \bar{M}^{-0.75}$$

$$\text{For PMMA [28]: } [\eta] = 6.27 \cdot 10^{-5} \bar{M}^{-0.76}$$

The number of the N,N-diethyldithiocarbamate group bonded at polystyrene end was determined by average-molecular weight and UV spectrum in comparison with that of BDC [λ_{max} 282 nm and $\epsilon=10500$ in cyclohexane].

RESULTS AND DISCUSSION

Photopolymerizations with BEDC, BDC, XEDC and XDC

Figs. 1 and 2 show the time-conversion and time- \bar{M} relations in the photopolymerizations of St and MMA, respectively, by BEDC, BDC, XEDC and XDC as photoinitiaters.

From these figures, the yield and \bar{M} of the polymers formed are observed to increase as a function of reaction time, indicating that the polymerizations proceed via a living radical mechanism in homogeneous system[20]. Similar results were reported already for the photopolymerizations of St and MMA with tetraethylthiuram disulfide[19,20], and for the polymerization of MMA with phenylazotriphenylmethane[20], in which the time- \bar{M} relations were observed to increase from an original point with the time.

The time- \bar{M} relation observed for the St polymerization with BDC is similar to the above cases reported, but that found for the other photoinitiaters does not cross the original point, i.e. the extent of increasing in \bar{M} s against the time decreases. This reason seems to come from that a part of the polymer chain ends effective to a living radical propagation is destroyed.

As is shown in Figs.1 and 2, when the concentration of the $(C_2H_5)_2NCSS-$ end group in BDC and XDC used was selected to be iden-

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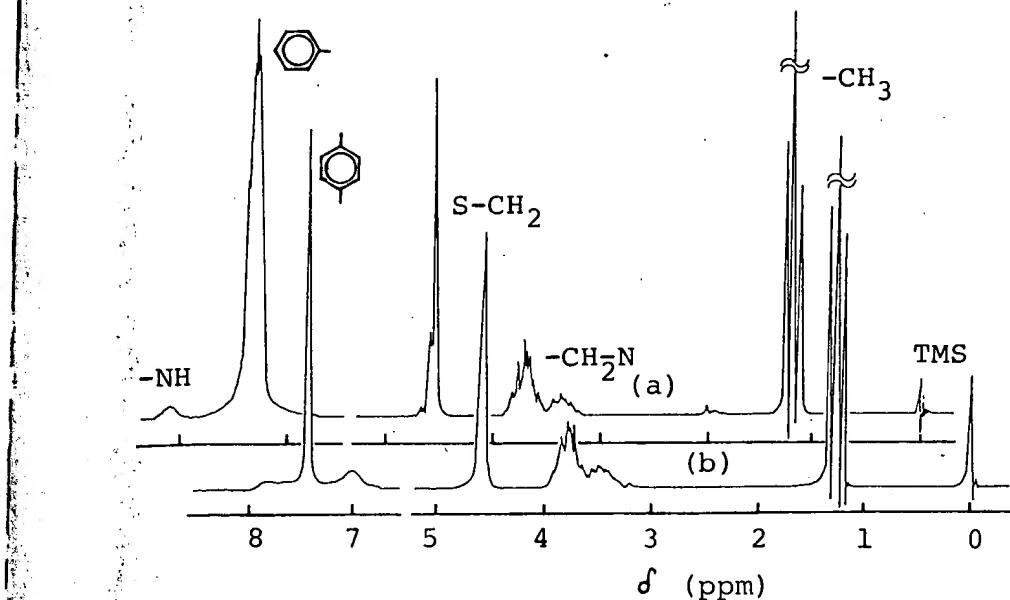


Fig. 1 H-NMR spectra of BEDC(a) and XEDC(b)

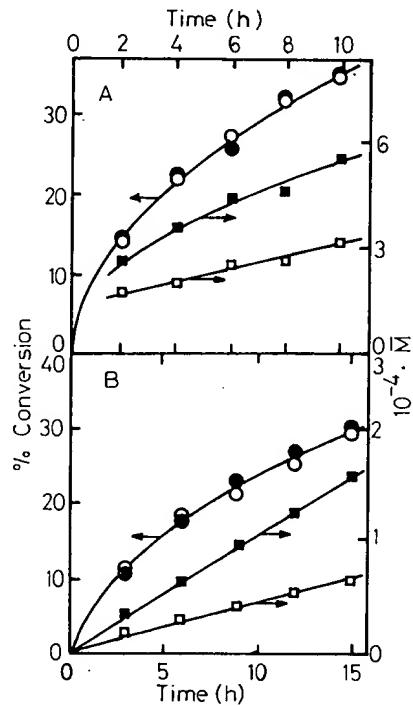


Fig. 2 Time-conversion and time- \bar{M} relations in photopolymerization of St with BEDC, XEDC, BDC and XDC as photoinitiators;
 A: $[BEDC]=2.0 \cdot 10^{-2} \text{ mol/l}$ (○, □)
 $[XEDC]=1.0 \cdot 10^{-2} \text{ mol/l}$ (●, ■)
 B: $[BDC]=7.8 \cdot 10^{-3} \text{ mol/l}$ (○, □)
 $[XDC]=3.8 \cdot 10^{-3} \text{ mol/l}$ (●, ■)
 $[St]=6.9 \text{ mol/l}$ in benzene at 30°C .

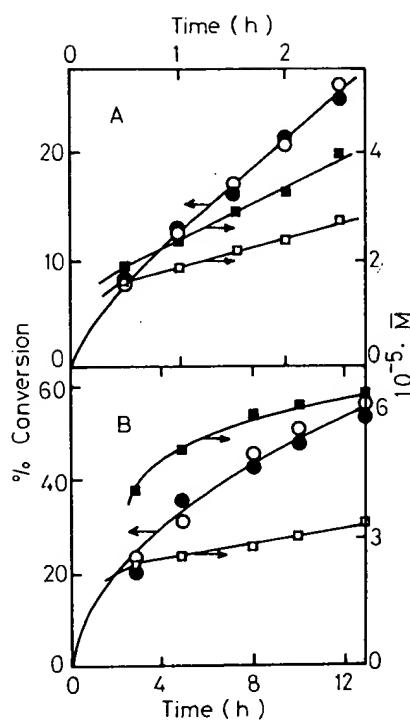


Fig. 3 Time-conversion and time- \bar{M} relations in photopolymerization of MMA with BEDC, XEDC, BDC and XDC as photoinitiaters;
 A: $[BEDC] = 1.0 \cdot 10^{-3} \text{ mol/l}$ (\circ , \square),
 $[XEDC] = 0.5 \cdot 10^{-3} \text{ mol/l}$ (\bullet , \blacksquare),
 B: $[BDC] = 7.9 \cdot 10^{-3} \text{ mol/l}$ (\circ , \square),
 $[XDC] = 3.9 \cdot 10^{-3} \text{ mol/l}$ (\bullet , \blacksquare),
 $[MMA] = 2.8 \text{ mol/l}$ at 30°C in benzene.

tical, i.e. $[BDC] = [XDC]/2$, the observed time-conversion relations for both BDC and XDC are quite identical each other, indicating that all the $(C_2H_5)_2NCSS-C$ bonds in XDC and XDC-polymer may dissociate photochemically with a probability similar to those in BDC and BDC-polymer into radicals which have identical reactivities. Similar results were also obtained for photopolymerizations with BEDC and XEDC.

However, the \bar{M} s of the polymers obtained with XDC are always two times larger than those with BDC. In the case of XEDC, the increase in \bar{M} s is somewhat less than two times of the \bar{M} s obtained with BEDC. This may be due to that a part of the effective polymer chain end is deactivated.

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To confirm whether these polymerizations proceed via a living radical mechanism, the number of the end groups of the polymers produced in photopolymerizations of St with BDC and XDC was determined. The results are shown in Tables 1 and 2.

From these tables, although the \bar{M}_n s of the polymers produced by BDC and XDC increase with the time, the number of the $(C_2H_5)_2NCSS-$ end groups per one polymer molecule are found to be almost constant (1.0 for BDC and 2.0 for XDC) independent of the reaction time. These results strongly suggest that the polymerizations with BDC and XDC proceed via a living mono- and biradical polymerization mechanisms, respectively [see eq.(12)].

Chain Extension Reactions of the Poly(St)s Obtained by BEDC and XEDC

Okawara and coworkers[29] have reported that the N-ethyl-dithiocarbamate ester group in the polymer of St is easily hydrolyzed with some nucleophiles as sodium hydroxide and dimethylamine to the thiol group which is then oxidized, and it also forms a chelate bond with divalent metal ions such as Cu(II) ion. If these reactions are applied to mono- and bifunctional polymers obtained by BEDC and XEDC, respectively, the following chain extension reactions seem to occur.

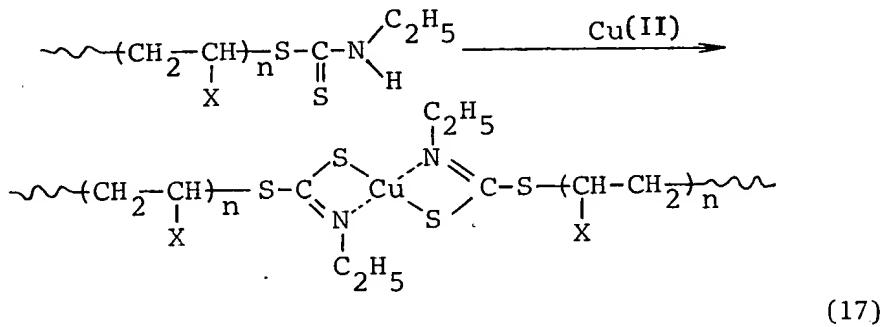
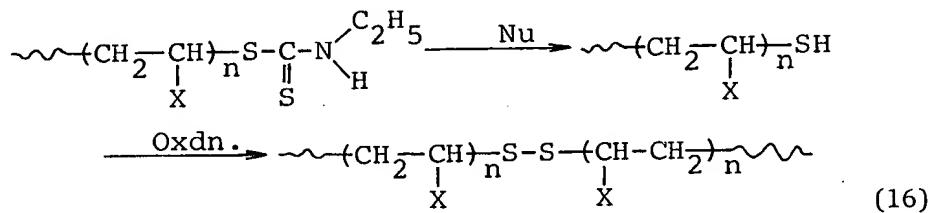


Table 1 Number of $(C_2H_5)_2NCSS-$ End Groups of the Polymers Produced in Photopolymerization of St with BDC and XDC^a)

Iniferter	Time (h)	$\bar{M} \times 10^{-4}$	Number of end group ^{b)}
BDC	3	2.1	0.9
	6	3.2	0.9
	9	4.3	1.0
	12	5.5	1.1
	15	6.3	1.0
XDC	3	3.8	1.8
	6	6.3	1.7
	9	9.5	1.9
	12	12.2	2.0
	15	15.4	2.0

a) Polymerization conditions; $[BDC]=7.8 \cdot 10^{-3}$ mol/l, $[XDC]=3.8 \cdot 10^{-3}$ mol/l, $[St]=6.9$ mol/l in benzene at $30^\circ C$.

b) The numbers of the $(C_2H_5)_2NCSS-$ end group per polymer molecule was determined from data of UV and \bar{M} .

Table 2 \bar{M}_n , \bar{M}_w , \bar{M}_w/\bar{M}_n and Number of $(C_2H_5)_2NCSS-$ End Groups of the Polymers Produced in Photopolymerization of St with BDC at $30^\circ C$ ^a)

Time (h)	$\bar{M}_n^b)$ $\times 10^{-4}$	$\bar{M}_w^b)$ $\times 10^{-4}$	\bar{M}_w/\bar{M}_n	Number of end group ^{c)}
2	0.7	1.2	1.7	0.9
4	1.1	2.3	2.2	0.8
8	1.7	4.5	2.7	1.0
12	2.0	6.8	3.4	1.1

a) Polymerization condition; $[St]=7.2$ mol/l, $[BEDC]=7.7$ mol/l.

b) Determined by gel permeation chromatography.

c) The number of the $(C_2H_5)_2NCSS-$ end group per one molecule was determined from both data of UV and \bar{M}_n .

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The results of the reactions with nucleophiles are shown in Table 3. The polymers with one and two thiol groups bonded at the chain ends were not isolated, but the chain extension reaction of the polymers was observed to occur through a disulfide bond formation. When the monofunctional polymer obtained by BEDC was used, the \bar{M} of the polymer obtained after reaction increases about two times as compared with that before reaction. However, in the cases of the bifunctional polymers obtained by XEDC, their \bar{M} s increase about 3-5 times rather than those before reaction.

Similar results were also obtained for chain extension reactions by a chelate bond formation as is shown in Table 4. If the polymers consist of mono- and bifunctional structure and the reactions occur completely, the \bar{M} must increase to two times and infinite quantity, respectively. As is seen from Tables 1 and 2, the observed functionalities of the polymers are somewhat lower than those expected (1.0 and 2.0 for BEDC- and XEDC-polymers, respectively). Therefore, the observed results (Tables 3 and 4) seem to come from these reasons.

Block Copolymerizations — Synthesis of AB and ABA Block Copolymers

Table 5 shows the results of block copolymerizations of MMA with the polymers of St obtained by BDC and XDC (BDC-PSt and XDC-PSt) as mono- and bifunctional polymeric photoiniferters, respectively. From this table, when the \bar{M} s of BDC-PSt and XDC-PSt increased, i.e. the concentration of the end group decreased, the yields of MMA polymerized were observed to decrease. However, the yields of the block copolymers with XDC-PSt (~90%) were higher than those with BDC-PSt (~70%).

To synthesize AB and ABA block copolymers, the polymers obtained by BDC or BEDC and XDC or XEDC as photoiniferters were used as mono- and bifunctional polymeric photoiniferters, respectively of the polymerizations of second monomers. The results are shown in Table 6.

From comparison of the \bar{M} s of the block copolymers determined (see footnote of Table 6) with those calculated, AB and ABA block

Table 3 Chain Extention Reaction of BEDC- and XEDC-Polymers by Disulfide Bond Formation^{a)}

Polymer	Before reaction $\bar{M} \cdot 10^{-4}$	After reaction $\bar{M} \cdot 10^{-4}$	\bar{M} / \bar{M}_0
BEDC-PSt	2.5	4.2	1.7
XEDC-PSt	2.6	6.3	2.4
XEDC-PSt	4.6	26.2	5.7
XEDC-PSt ^{b)}	4.6	16.2	3.5
XEDC-PSt ^{c)}	4.6	23.8	5.2

a) Reaction conditions: polymer 0.3g in dioxane(10ml) was reacted with 10% aq. NaOH(1ml) at 60°C for 8h, and then oxidized by air at room temp. for 1 day.

b) 50% aq. $(CH_3)_2NH$ was added as nucleophile instead of aq. NaOH.

c) SeO_2 (20mg) was added as oxidation catalyst.

Table 4 Chain Extention Reaction of BEDC- and XEDC-Polymers by Chelate Formation^{a)}

Polymer	Before reaction $\bar{M} \cdot 10^{-4}$	After reaction $\bar{M} \cdot 10^{-4}$	\bar{M} / \bar{M}_0
BEDC-PSt	2.1	3.6	1.7
BEDC-PSt	2.5	4.4	1.8
XEDC-PSt	2.6	12.7	4.9
XEDC-PSt ^{b)}	2.6	14.7	5.6
XEDC-PSt	4.6	18.9	4.1

a) Chelating reaction: polymer 0.2g, $Cu(CH_3COO)_2$ 0.2g, DMF 5ml, at room temp. for 2 days.

b) Chelating reaction was performed for 6 days.

Table 5 Block Copolymerization of MMA with BDC- and XDC-PSts^{a)}

Polymeric photoiniferter(M_1)	$\bar{M} \cdot 10^{-4}$	Total yield (g)	Fractions extracted (%)		
			Homo-poly(M_1)	Homo-poly(M_2)	Block copolymer
BDC-PSt	3.2	0.78	7	15	78
	4.3	0.64	8	16	76
	5.5	0.56	9	17	74
	6.3	0.50	13	16	71
	8.6	0.42	16	20	64
XDC-PSt	3.8	1.10	0	8	92
	6.3	0.99	2	9	89
	12.0	0.58	6	6	88
	15.0	0.49	0	8	92
	28.0	0.45	9	1	90

a) Polymerization at 30°C under irradiation of UV light from a distance of 10cm; polymeric photoiniferter 0.2g, $[MMA]=4.7\text{mol/l}$ in benzene.

Table 6 Results of Block Copolymerizations^{a)}

ion	$\overline{M} / \overline{M}_0$
	1.7
	2.4
	5.7
	3.5
	5.2

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	1.7
	1.8
	4.9
	5.6
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CO_2	$\overline{M} / \overline{M}_0$
	1.7
	1.8
	4.9
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	78
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Table 6 Results of Block Copolymerizations a)

Polymeric photooiniferter (M ₁)	Functional monomer (M ₂)	Second monomer (M ₁)	Time (h)	Total yield (g)	Fractions extracted		Type of block copolymer (calcd. $\overline{M} \cdot 10^{-5}$)				
					Homopolymer Wt (%) $\overline{M} \cdot 10^{-5}$	Homom ₂ polymer Wt (%) $\overline{M} \cdot 10^{-5}$					
BEDC-PSt	1	MMA(4.7)	3	0.59	17.8	0.24	29.1	3.7	53.1	4.0	AB (3.9)
BEDC-PMMA	1	St (6.5)	6	0.29	41.0	1.56	12.8	1.3	46.2	3.0	AB (2.9)
XEDC-PSt	2	MMA(4.7)	3	0.79	8.7	0.36	25.0	1.7	66.3	3.8	ABA (3.8)
XEDC-PMMA	2	St (6.5)	6	0.29	19.4	2.36	16.4	1.2	64.2	4.3	ABA (4.8)
BDC-PSt	1	MMA(4.7)	3	0.78	7.0	0.32	15.0	2.4	78.0	2.4	AB (2.7)
BDC-PMMA	1	St (6.5)	6	0.33	35.0	0.35	23.0	1.0	42.0	1.3	AB (1.4)
XDC-PSt	2	MMA(4.7)	3	0.99	2.0	0.63	9.0	2.5	89.0	4.9	ABA (5.6)
XDC-PMMA	2	St (6.5)	6	0.34	31.0	0.65	19.0	0.9	50.0	2.2	ABA (2.5)

a) Polymerization at 30°C under irradiation of UV light from a distance of 10cm; polymeric photoiniferter 0.2g, monomer 3ml, benzene 2ml.

b) Calculated by the following equation:

$$[\eta]_{\text{block}}^{2/3} = x(8.5 \cdot 10^{-5} \overline{M}^{0.75})^{2/3} + (1-x)(6.27 \cdot 10^{-5} \overline{M}^{0.76})^{2/3}$$

x: weight fraction of St unit.
c) Determined by comparing of molecular weight calculated from $[\eta]_{\text{block}}$ with that calculated for AB or ABA block copolymer.

copolymers were produced when the polymers obtained by BDC or BEDC and XDC or XEDC were used as mono- and bifunctional polymeric photoinitiaters, respectively.

By using this technique, we have recently synthesized the AB and ABA block copolymers consisting of random and alternating copolymer sequences, and the star-type block copolymers. These results will be described in a future publication.

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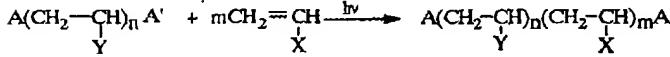
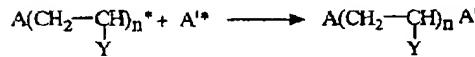
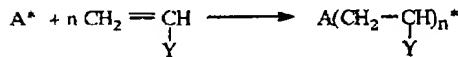
SILOXANE INIFERTERS AND THEIR USE IN MAKING VINYL/SILOXANE BLOCK COPOLYMERS

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INTRODUCTION

Otsu provided the initial framework of the study of iniferters¹ (initiator - transfer agent - terminator), delineating their ability to dissociate when irradiated to form highly-active initiating radicals A* and much less active terminating radicals A'*(Scheme 1). Reaction of the initiating radical with

Scheme 1



available reactive vinyl monomer, such as an acrylate or styrene, produces a growing polymer chain which is reversibly terminated by reaction with A'*. Since the new C-A' bond is approximately as labile as the A-A' bond, the new polymer chain, terminated by the A' group, has become a polymeric photoiniferter, capable of further reaction with a new monomer to produce a block copolymer.

Initial investigations of photoiniferters were directed mainly towards polymers in which vinyl-type monomers formed addition polymers such as poly(acrylates) and polystyrene (Otsu, et al.)². More recent studies, using macroiniferters, have expanded their scope to include siloxanes³, polyurethanes⁴, polyolefins⁵, poly(vinyl chloride)⁶, and various macromers⁷.

This paper describes the synthesis of novel siloxane iniferters and their use in making vinyl/siloxane block copolymers.

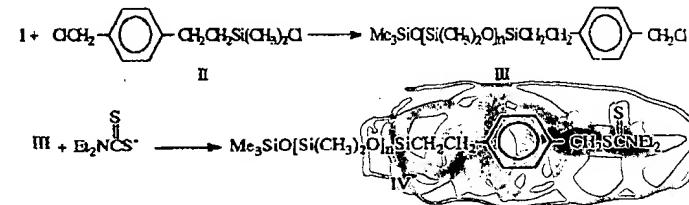
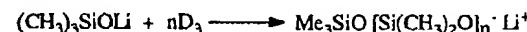
RESULTS AND DISCUSSION

In U. S. Patent No. 5,071,936⁸, S. Himori describes the preparation of polysiloxanes containing dithiocarbamate groups which can be used as siloxane-iniferters for the preparation of vinyl/silicone copolymers. The first step in the synthesis is the preparation of a halogenated polysiloxane, the halogen atoms of which can then be displaced with dithiocarbamate groups. In considering the rates of such nucleophilic substitutions, the halogen atoms are preferably chlorine or bromine. Polysiloxanes halogenated at one or both ends of the polymer chain are obtained by known methods in which living polymerization of either hexamethylcyclotrisiloxane, "D₃," or octamethylcyclotetrasiloxane, "D₄," is terminated with dimethylchlorosilane or tetramethylsiloxane to give polymers with one or two hydrogens bound to silicons at the termini, respectively. Platinum-catalyzed hydrosilylation with p-chloromethylstyrene yielded polysiloxanes with either one or two terminal aliphatic chlorine atoms. Himori also points out that polysiloxanes bearing non-terminal chloromethyl groups can be

obtained by ring opening copolymerizations of D₃ or D₄ with chlorocyclosiloxanes, or by hydrosilylation of polysiloxanes containing hydrogens bound to non-terminal silicons such as are commercially available (e.g., SH-1107 from Toray Silicone or KF-99 from Shin-etsu Silicone).

Polysiloxanes with terminal halogen atoms are prepared by reacting D₃ with lithium trimethylsilanoate, Me₃SiOLi, at 0° C in THF. When all of the D₃ is consumed, 1-(dimethylchlorosilyl)-2-(p-chloromethylphenyl)ethane (II) was added and the resulting mixture was stirred at room temperature, terminating the anionic polymerization. Removal of precipitated lithium chloride and any unreacted end-capper gave a polysiloxane with a terminal chloromethyl group (III), as per Scheme 2. The experimental details are published elsewhere⁹.

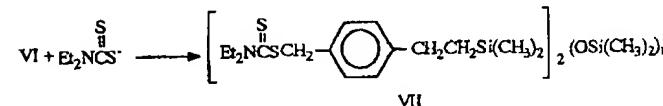
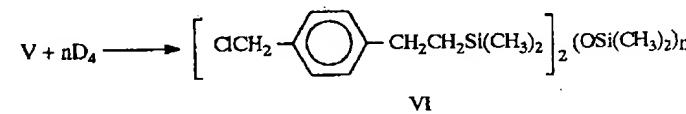
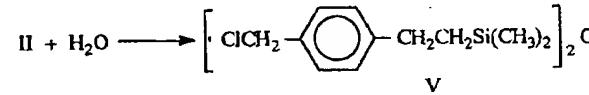
Scheme 2



Substitution of chlorine by dithiocarbamate takes place at temperatures between about 50° C and about 90° C in a solvent such as toluene, xylenes, or ethyl acetate under nitrogen. A phase transfer catalyst such as trioctylmethylammonium chloride or tetrabutylammonium chloride is often used advantageously.

Polysiloxanes halogenated at both chain ends are prepared via the symmetrical *bis*-chloro siloxane V as shown in Scheme 3. Hydrolytic coupling of chlorosilane II gave V, which also acts as an endcapper in the acid-catalyzed polymerization of cyclosiloxanes such as D₄. In this case, D₄, the endcapper V, and a small amount of sulfuric acid catalyst were stirred and heated under nitrogen at 90° C in the presence of carbon black (as an acid adsorbent). Filtration and stripping

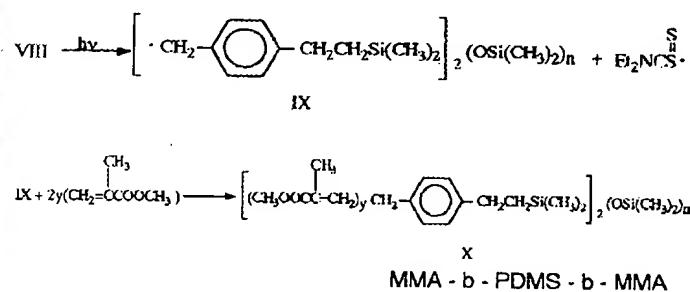
Scheme 3



gave the desired *bis*-chlorinated polysiloxane VI. Displacement of chlorine with N,N-diethyldithiocarbamate gave the macro di-iniferter VII, in good yield.

Siloxane iniferters are used to make block and graft copolymers by irradiating them, usually with UV, in the presence of a free substituted vinyl (i.e., ethylenically-unsaturated) compounds which include the esters, amides, nitriles, etc., of (meth)acrylic acids, styrene derivatives, vinyl esters, allylic compounds, and the like. (Meth)acrylic acid esters of perfluoroalkylsulfonamido alcohols can also be used. Copolymerization of the monomer and the polysiloxane iniferter takes place in non-reactive UV-transparent solvent such as methyl ethyl ketone or ethyl acetate. Polysiloxane monoiniferters such as those described in Scheme 2 form block copolymers having AB, CAB, etc., architecture. Diiniferters (Scheme 3) form block copolymers of the ABA, CABAC, etc., type. In both cases, "B" represents the polydimethylsiloxane block, and "A," "C," etc., represent blocks from the vinyl monomers. A typical reaction, in this case with methyl methacrylate, is shown in Scheme 4.

Scheme 4



A number of polysiloxane block copolymers are discussed in U.S. Patent No. 5,057,619. Table I shows some compositions and their physical properties.

The vinyl - polysiloxane block and graft copolymers are easily prepared from the polysiloxane iniferter. Control of the ratio of vinyl to polysiloxane blocks allows rather precise tailoring of copolymer composition. Thus, unique materials that exhibit the combined properties of dissimilar polymers are possible, which may find utility in a wide range of applications, such as low adhesion backsizes, impact-resistant materials, fabric protectors, etc.

Table I

Copolymer Composition, °C	Mn	Mw	Mw / Mn	Tg,
MMA-b-PDMS-b-MMA	17,154	30853	1.761	-124 +105
(MA/AA) _x -b-PDMS-b-(MA/AA) _x	22,200	53,000	2.39	-126 +60
HEA-b-MMA-b-PDMS-b-MMA-b-HEA	13,162	20,644	1.56	-120 +107
MMA-b-PDMS	15,416	20,394	1.33	-124 +106

MMA = Methyl Methacrylate
MA = Methyl Acrylate
AA = Acrylic Acid
HEA = 2-Hydroxy Ethyl Acrylate

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Polymer Design by Iniferter Technique in Radical Polymerization: Synthesis of AB and ABA Block Copolymers Containing Random and Alternating Copolymer Sequences

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ABSTRACT: The iniferter technique was applied to synthesis of the AB and ABA block copolymers containing various random and alternating copolymer sequences. Benzyl *N,N*-diethyldithiocarbamate (BDC), *p*-xylylene bis(*N,N*-diethyldithiocarbamate) (XDC) and 1,2,4,5-tetrakis(*N,N*-diethyldithiocarbamylmethyl)benzene (DDC) were used as mono-, bi- and tetra-functional photoiniferters, respectively. The photopolymerizations with BDC and XDC proceeded via a living radical mechanism, and gave soluble mono- and bifunctional polymers (photoiniferters); respectively. However, DDC induced living radical polymerization of styrene with gelation. When various polymers and copolymers obtained by BDC and XDC were used as polymeric photoiniferters, the AB and ABA block copolymers containing random copolymer sequences were obtained in high yields. Similarly the alternating copolymerization of isobutyl vinyl ether with maleic anhydride in the presence of the alternating copolymers such as styrene and diisopropyl fumarate, which were obtained by BDC and XDC, as polymeric photoiniferters was found to give the AB and ABA block copolymers consisting of alternating copolymer sequences. DDC and the polymers and copolymers obtained by DDC could also act as an excellent cross-linking agent.

KEY WORDS Radical Polymerization / Living Radical Polymerization / Initiator / Iniferter / Iniferter Technique / Polymer Design / Block Copolymer /

The structure control of the producing polymer, *i.e.*, the reactivity control of the reacting monomer, in radical polymerization is now the most important problem to design and architect the polymer structure. To approach this purpose, we have recently proposed a concept of initiator-transfer agent-terminator (iniferter)¹ for designing of the polymer chain end structure, and simultaneously a new model for living radical polymerization in homogeneous system by using iniferters such as phenylazotriphenylmethane² and some organic sulfur compounds.²⁻⁵ These ideas are summarized briefly as follows.

The Concept of Iniferter

The polymer formation in radical polymerization of vinyl monomers (M) initiated by an initiator

(R-R') is expressed by eq 1, if no chain transfer reactions occur and mutual termination proceeds only by recombination.



In this case, radical polymerization gives a polymer with two initiator fragments at its chain ends. However, in ordinary radical polymerization of many monomers, the termination by disproportionation and the chain transfer reactions have been known to occur importantly, *i.e.* the number of initiator fragments per one polymer molecule is always less than 2.

So if we use initiators which have very high reactivities for chain transfer to the initiator and/or primary radical termination in order to avoid ordinary bimolecular terminations, it is expected to be

obtained a polymer with two initiator fragments at its chain ends (eq 2).



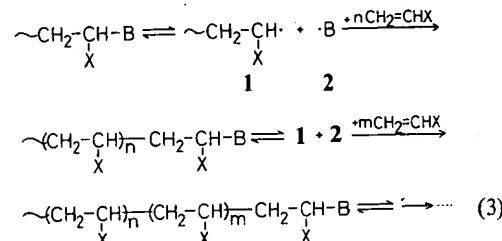
Therefore, these radical polymerizations may simply be considered as an insertion reaction of monomer molecules into the R-R' bond of the initiator leading to a polymer with two initiator fragments at its chain ends, as well as the special case shown in eq 1. For initiators with these functions we proposed to call iniferter¹ in analogy with "inifer" named by Kennedy⁷ in cationic polymerization. Many radical initiators which have been used are also expected to serve as an iniferter if monomers and polymerization conditions are selected.

As is seen from eq.2, the polymers obtained by iniferter still contain its fragments at the polymer chain ends. If these iniferter fragments can have further function as an iniferter, such a polymerization may proceed *via* a living radical mechanism (see later), and the polymers isolated have always the same end groups which can act as iniferter to give the propagating polymer radical. Therefore, the choice of such iniferters in vinyl polymerization seems to open a novel route for synthesizing of various types of polymers such as functional, telechelic, block and graft polymers *via* a radical polymerization technique.

From a viewpoint of the tailor-made polymer synthesis, the iniferters can be classified into several types; mono-, bi-, tri- or polyfunctional iniferter; thermal or photoiniferter; monomeric or polymeric iniferter etc.⁸ Recently, some sulfur compounds having *N,N*-diethyldithiocarbamate group were found to serve as an excellent photoiniferter and induced living radical polymerization of vinyl monomers.¹⁻⁶ When benzyl *N,N*-diethyldithiocarbamate (BDC) and *p*-xylylene bis(*N,N*-diethyldithiocarbamate) (XDC) (see later) were used as mono- and bifunctional photoiniferters, the polymers which can serve as mono- and bifunctional polymeric photoiniferters, respectively, were produced.⁶ Therefore, the polymerization of second monomers with these mono- and bifunctional polymeric photoiniferters was found to become an excellent route for synthesizing of the AB and ABA block copolymers, respectively.⁶

A New Model for Living Radical Polymerization in Homogeneous System

As described above, if the end groups of the polymers obtained by radical polymerization using certain iniferters still have an iniferter function, these radical polymerization is expected to proceed *via* a living mechanism even in homogeneous system according to eq 3.²



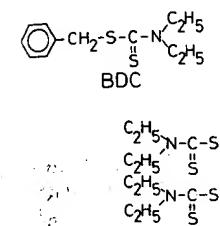
The propagating polymer chain ends, which act as an infirter, can dissociate thermally or photochemically into a propagating radical (1) and a small radical (2) which must be stable enough not to initiate new polymer chain. Therefore, this less reactive small radical may readily undergo recombination with a more reactive propagating radical to give a polymer with the identical end groups, *i.e.*, the monomer molecules are inserted into this infirter bond of the propagating polymer chain end. So, if these radical dissociation, monomer-addition and recombination cycles are repeated, such a radical polymerization may proceed *via* a living mechanism even in homogeneous system.

Such results were observed for radical polymerizations with phenylazotriphenylmethane,² azobisisdiphenylethanes,⁹ tetraphenylmethanes,⁸ as thermal initiators and with some organic sulfur compounds^{2-6,8} as photoinitiators. Among these initiators, the compounds having *N,N*-diethylthiocarbamate groups were investigated in detail.

In previous works,^{5,6} it has also been found that BDC and XDC can induce living mono- and biradical polymerizations, respectively, and produce efficiently the AB and ABA block copolymers by using the respective polymeric photoinitiaters. Moreover, when 1,2,4,5-tetrakis(*N,N*-diethylthiocarbamylmethyl)benzene (DDC) was used as a tetrafunctional photoinitiator of living radical polymerization of methyl methacrylate, a star polymer was produced.⁹

To extend further these iniferter technique to new polymer synthesis, living radical polymerizations

with BDC, XDC, a tetrafunctional phot investigated, and ob copolymers containing copolymer se are described in this



EXI

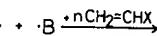
BDC,⁶ XDC,⁶ ar reaction of benzyl and 1,2,4,5-tetrachlor with sodium *N* ethanol, and then crystallization. Sty (MMA), vinyl ace were used after ord

Photopolymerization of monomer XDC, and DDC (BDC-P, XDC-P, tained with above benzene at 30°C under SHL-100 UV lamp polymerization for isolated by pouring methanol. The precipitating the anol three times, f

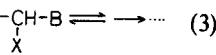
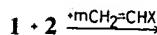
The separation obtained into the polyunblocked polymer by extraction with CHCl_3 for the copolymer for PVAc, and ac block copolymer in benzene solution of CH_3OH . In the case of isobutyl vinylidene (MAN) in the PSt as photoinitiator

radical Polymerization in

the end groups of the polymerization using an iniferter function, is expected to proceed in homogeneous sys-



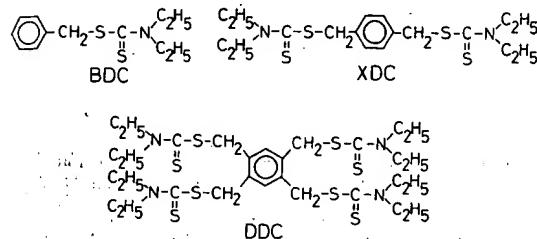
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chain ends, which act thermally or photo-
ically as radical (1) and a stable enough not to undergo repropagation radical to radical end groups, *i.e.*, inserted into this living polymer chain end. In monomer-addition repeated, such a radical *via* a living mechanism.

for radical polymerization¹ of methane,² azobisisobutyranes,³ as thermal organic sulfur compounds. Among these initiating *N,N*-diethyldithiocarbamate investigated in detail. It has been found that mono- and biradicals, and produce block copolymers by radical photoiniferter. *N,N*-diethyldithiocarbamate (BDC) was used as a radical of living radical methacrylate, a star polymer technique to new radical polymerizations

with BDC, XDC, and DDC as mono-, bi-, and tetrafunctional photoiniferters, respectively, were investigated, and obtained the AB and ABA block copolymers containing various random and alternating copolymer sequences. The results obtained are described in this paper.



EXPERIMENTAL

BDC,⁶ XDC,⁶ and DDC⁹ were prepared by the reaction of benzyl chloride, *p*-xylylene dichloride and 1,2,4,5-tetrachloromethylbenzene, respectively, with sodium *N,N*-diethyldithiocarbamate in ethanol, and then purified by distillation or recrystallization. Styrene (St), methyl methacrylate (MMA), vinyl acetate (VAc), and other reagents were used after ordinary purifications.

Photopolymerizations were carried out in the presence of monomeric photoiniferters (BDC, XDC, and DDC) or polymeric photoiniferters (BDC-P, XDC-P, and DDC-P) which were obtained with above monomeric photoiniferters in benzene at 30°C under irradiation with a Toshiba SHL-100 UV lamp from a distance of 10 cm. After polymerization for a given time, the polymer was isolated by pouring the polymerization mixture into methanol. The polymers were then purified by reprecipitating their benzene solutions into methanol three times, followed by drying in vacuum.

The separation of the whole polymers thus obtained into the polymeric iniferter initially used and unblocked polymer or copolymer was carried out by extraction with benzene-cyclohexane (7:3 by vol) for the copolymers of St with MMA, methanol for PVAc, and acetonitrile for PMMA. Then, the block copolymer was isolated by pouring the benzene solution of the residual polymers into methanol. In the case of alternating copolymerization of isobutyl vinyl ether (IBVE) with maleic anhydride (MAn) in the presence of BDC-PSt or XDC-PSt as photoiniferters, the whole copolymer ob-

tained was hydrolyzed with 5% sodium hydroxide aqueous solution, followed by neutralization with hydrochloric acid. Then the block copolymers were extracted with methanol-water (2:1 by vol). Similarly, the block copolymers consisting of alternating copolymers of St and diisopropyl fumarate (DiPF) with those of IBVE and MAn were extracted with benzene, followed by hydrolysis and neutralization.

RESULTS AND DISCUSSION

Living Radical Polymerization of St with BDC, XDC, and DDC as Photoiniferters

Figures 1 and 2 show the time-conversion and time- \bar{M} relations in the photopolymerization of St with BDC, XDC, and DDC as mono-, bi-, and tetrafunctional photoiniferters in which the concentration of the *N,N*-diethyldithiocarbamate

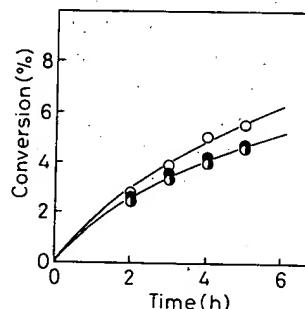


Figure 1. Time-conversion relations in photopolymerization of St with BDC, XDC, and DDC in benzene at 30°C: [St] = 6.9 mol l⁻¹, [BDC] = 5.4 × 10⁻⁴ mol l⁻¹ (●); [XDC] = 2.6 × 10⁻⁴ mol l⁻¹ (○); 1.3 × 10⁻⁴ mol l⁻¹ (□).

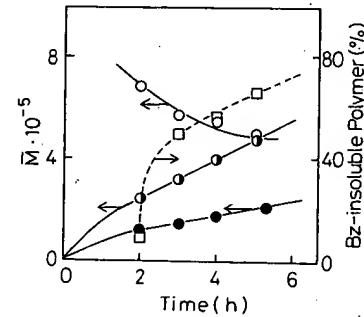


Figure 2. Time- \bar{M} relations in photopolymerization of St with BDC (●), XDC (○), and DDC (□), yield of benzene-insoluble polymer; ○, \bar{M} of soluble polymer. The concentrations are the same as those in Fig. 1.

group was kept constant: $[BDC] = [XDC]/2 = [DDC]/4$.

As is seen from Figure 1, the time-conversion relations observed by BDC and XDC are identical to one another, indicating that all of these *N,N*-diethyldithiocarbamate groups show identical reactivity for radical polymerization. However, the polymer yields obtained by DDC are somewhat higher than the above relation. This result seems to be originated from the gel effect, because the polymerization proceeded with gelation, *i.e.*, the formation of insoluble polymers (Figure 2). In fact, the polymerization of MMA with DDC proceeded without gelation and the identical reactivity relationship of all *N,N*-diethyldithiocarbamate groups was observed to hold between BDC, XDC, and DDC.⁹

From Figure 2, the \bar{M} values of the polymers obtained by BDC and XDC are also observed to increase as a function of reaction time, indicating that these polymerizations proceeded *via* a living radical mechanism.²⁻⁶ It is noted that the \bar{M} values of the polymers obtained by XDC are just two times higher than those by BDC. From this result, it is concluded that the polymerizations of St by BDC and XDC proceed according to the ideal living mono- and biradical mechanisms.

As described above, the polymerization of St with DDC proceeded with gelation and the resulting benzene-insoluble polymer did not soluble in any solvent, suggesting the formation of a cross-linked polymer. However, the intrinsic viscosities of the benzene-soluble polymers isolated decreased with reaction time. The results observed for the St polymerization were different from those for the polymerization of MMA with DDC,⁹ in which the incompletely soluble polymers were produced independent of polymerization time. When a small amount of tetraethylthiuram disulfide, however, was added to the polymerization of St with DDC, no gelation occurred and the soluble star polymer was isolated by fractionation. The results will be published in a next paper.

Synthesis of AB and ABA Block Copolymers Containing a Random Copolymer Sequence

To prepare the mono- and bifunctional polymeric photoiniferter containing random copolymer sequence, the photocopolymerizations of St with MMA were carried out in the presence of BDC and

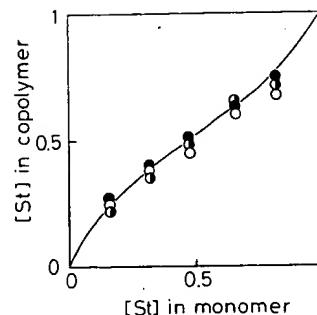


Figure 3. Copolymer composition relations in photopolymerization of St (M_1) with MMA (M_2) with BDC (\circ), XDC (\bullet), and azobisisobutyronitrile (\bullet) in benzene at 30°C: $[BDC] = 9.6 \times 10^{-3}$ mol l^{-1} ; $[XDC] = 4.8 \times 10^{-3}$ mol l^{-1} ; —, calculated curve as $r_1 = 0.57$ and $r_2 = 0.46$.

XDC, respectively, in benzene at 30°C. The monomer feed-copolymer composition relations observed with both photoiniferter were in good agreement with those with azobisisobutyronitrile as an ordinary radical initiator, as is shown in Figure 3. This result strongly suggests that these radical copolymerizations by BDC and XDC proceeded *via* a free radical mechanism.

Since the PSt prepared by BDC and XDC have been found to contain one and two *N,N*-diethyldithiocarbamate end groups,⁶ respectively, the copolymers thus obtained are expected to serve similarly as mono- and bifunctional photoiniferter. These are supported by the facts that all of copolymerizations proceeded *via* a living radical mechanism, and the intrinsic viscosity of the copolymer [XDC-P(St-MMA)] obtained by XDC was higher about a factor of two than that [BDC-P(St-MMA)] obtained by BDC under identical conditions (see Table I).

The time-conversion relation observed in the photopolymerization of VAc with XDC-P(St(45)-MMA) (0.2 g) as a bifunctional polymeric photoiniferter at 30°C is shown in Figure 4, in which the plots of the yields and $[\eta]$ of the block copolymers isolated *versus* reaction time are also indicated. From this figure, the yields of both total and blocked polymers and the $[\eta]$ s of the block copolymers are observed to increase with increase of the reaction time, and the block copolymers containing a random copolymer sequence are produced

Table I. 1

Copolymeric photoiniferter

XDC-P[St (66)-MMA]
XDC-P[St (45)-MMA]
XDC-P[St (35)-MMA]
XDC-P[St (66)-MM]
XDC-P[St (45)-MM]
XDC-P[St (35)-MM]
BDC-P[St (45)-MM]
XDC-P[St (45)-MM]
DDC-P[St (45)-MM]
BDC-P[St (>95)-IB]
XDC-P[St (>95)-IB]
DDC-P[St (>95)-IB]
XDC-P[St-BD]
XDC-P[St (94)-VAc]
XDC-P[St (>95)-VAc]

^a Photopolymerized 10.4 mol l^{-1} .

^b Indicated the com chloride.

^c Values in parenthesis.

^d Values in parenthesis.

^e Cross-linked poly

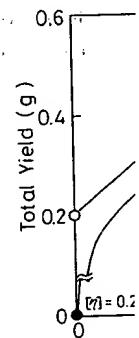


Figure 4. Time-total yield in photopolymerization of VAc with XDC-P[St(45)-MMA] as photoiniferter, 0.2 g; VAc, $[\eta]$ of the block copolymer.

in higher yields than polymeric photoiniferter increase from 0.29 dl to 0.45 dl g⁻¹ for 13 h.

Table I. Results of polymerizations of vinyl monomers with copolymeric photoinitiaters^a

Copolymeric photoinitiaters ^b	Second monomer (M ₂) ^c	Time h	Total yield g	Fraction isolated/wt%		
				Copolymer	HomoPM ₂	Block copolymer ^d
XDC-P[St(66)-MMA]	VAc (7.8)	8	0.43	11.1	15.6	73.3
XDC-P[St(45)-MMA]	VAc (7.8)	8	0.48	7.4	14.4	78.8 (0.69)
XDC-P[St(35)-MMA]	VAc (7.8)	8	0.48	5.1	13.2	81.7
XDC-P[St(66)-MMA]	AA (10.4)	0.3	0.38	3.3	8.9	87.9
XDC-P[St(45)-MMA]	AA (10.4)	0.3	0.38	4.1	14.9	81.0
XDC-P[St(35)-MMA]	AA (10.4)	0.3	0.32	6.7	18.5	74.8
BDC-P[St(45)-MMA]	VAc (7.8)	5	0.36	22.7	22.4	54.9 (0.37)
XDC-P[St(45)-MMA]	VAc (7.8)	5	0.32	13.5	10.1	76.3 (0.66)
DDC-P[St(45)-MMA]	VAc (7.8)	5	0.46	0.0	7.8	92.2 ^e
BDC-P[St(>95)-IB]	MMA (6.7)	3	0.87	15.6	32.6	51.8
XDC-P[St(>95)-IB]	MMA (6.7)	3	0.83	15.0	18.7	66.3
DDC-P[St(>95)-IB]	MMA (6.7)	3	0.85	0.0	9.8	90.2 ^e
XDC-P[St-BD]	MMA (6.7)	3	1.21	14.1	20.6	65.3
XDC-P[St(94)-VAc]	MMA (6.7)	3	1.33	14.2	2.9	82.8
XDC-P[St(>95)-VC]	MMA (6.7)	3	1.00	8.6	12.3	79.1

^a Photopolymerized in benzene at 30°C. Copolymeric photoinitiator 0.2 g, [VAc] = 7.8, [MMA] = 6.7 and [AA] = 10.4 mol l⁻¹.

^b Indicated the compositions of monomer unit in the copolymers (in mol%). IB, isobutene; BD, butadiene; VC, vinyl chloride.

^c Values in parentheses indicated the monomer concentration (mol l⁻¹).

^d Values in parentheses indicated the $[\eta]$ values in benzene at 30°C.

^e Cross-linked polymer was produced.

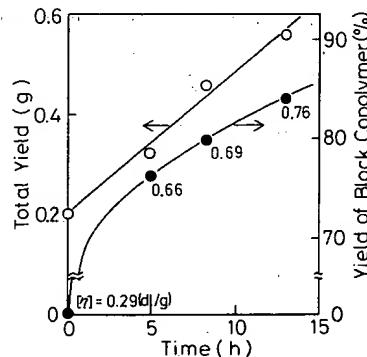


Figure 4. Time-total yield and time-block copolymer yield in photopolymerization of VAc with XDC-P[St(45)-MMA] as polymeric photoinitiator at 30°C: initiator, 0.2 g; VAc, 5 ml; benzene, 2 ml. Values indicate $[\eta]$ of the block copolymers isolated.

in higher yields than 75%. Further, $[\eta]$ for the copolymeric photoinitiator is also observed to increase from 0.29 dl g^{-1} to 0.76 dl g^{-1} after polymerization for 13 h.

Similar results were also observed for the polymerization of VAc with BDC-P[St(45)-MMA] as a monofunctional copolymeric photoinitiator. The $[\eta]$ (0.66 dl g^{-1}) of the block copolymer isolated from the VAc polymerization with XDC-P[St(45)-MMA] was about two times higher than that (0.37 dl g^{-1}) with BDC-P[St(45)-MMA], probably indicating that the following AB and ABA block copolymers containing random copolymer sequence were produced when mono- and bifunctional copolymeric photoinitiaters were used, respectively.

$(\text{St-}co\text{-MMA})_n - b - (\text{M}_3)_m$

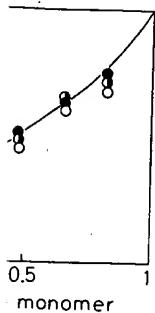
AB type

$(\text{M}_3)_m - b - (\text{St-}co\text{-MMA})_n - b - (\text{M}_3)_m$

ABA type

where M_1 , M_2 , and M_3 are St, MMA, and VAc, respectively.

Table I summarizes the results of the polymerizations of VAc, MMA, and acrylic acid (AA) using various random copolymers obtained from BDC, XDC, and DDC as photoinitiaters. In all cases, the block copolymers were isolated in high yields. When



position relations in photopolymerization of MMA (M_2) with BDC as a photoinitiator (●) in benzene at 30°C : $[BDC] = 10^{-3} \text{ mol l}^{-1}$; $[\text{MMA}] = 6.7 \text{ mol l}^{-1}$; $[\text{VAc}] = 7.8 \text{ mol l}^{-1}$; $[\text{AA}] = 10.4 \text{ mol l}^{-1}$; isolated curve as $r_1 = 0.57$ and $r_2 = 0.43$.

zene at 30°C. The monomer position relations observed were in good agreement with bisobutynonitrile as an initiator as is shown in Figure 3. It is suggested that these radical copolymer XDC proceeded via a

by BDC and XDC have one and two N,N -dimethyl groups,⁶ respectively, and are expected to serve as functional photoinitiaters. The facts that all of copolymerization of a living radical mechanism is viscosity of the copolymer obtained by XDC was higher than that [BDC-P[St(45)-MMA]] under identical conditions.

lation observed in the polymerization of VAc with XDC-P[St(45)-MMA] as polymeric photoinitiator is shown in Figure 4, in which $[\eta]$ of the block copolymer on time are also indicated. The yields of both total and the $[\eta]$ s of the block copolymer increase with increase of block copolymers containing random sequence are produced

the results are compared with respect to the functionality of photoiniferters used, the yields of block copolymers are in the order; mono- < bi- < tetrafunctional copolymeric photoiniferters. Similar to the results described above, the AB and ABA block copolymers containing a random copolymer sequence might be produced when mono- and bifunctional photoiniferters are used, respectively.

Since the polymer of MMA obtained with DDC as a tetrafunctional photoiniferter was recently found to contain a soluble star polymer,⁹ the copolymers of St with MMA or St with IB produced with DDC are also expected to contain a star polymers with a random copolymer sequence. Therefore, the polymerizations with the DDC copolymers were performed with gelation, and the cross-linked block copolymers were obtained in higher yields than 90%. Although a large portion of these copolymers was insoluble, their soluble fractions might be a star polymer containing a block copolymer sequence. This result might also suggest that these tetrafunctional polymeric photo-initiators can act as an excellent cross-linking agent.

Synthesis of Block Copolymers Containing Alternating Copolymer Sequence

Recently Bamford and Han¹⁰ have prepared some block copolymers with alternating copolymer

sequence through alternating copolymerization procedure in the presence of the initiator systems consisting of $Mn_2(CO)_{10}$ and the polymers having the reactive carbon-halogen bonds at their chain ends. This method seems to be similar to the present iniferter technique.

It has been well known that the electron-accepting monomer, such as $M\bar{A}n$, diethyl fumarate (DEF)¹¹ and DiPF,¹² can easily undergo alternating copolymerization with the electron-donating monomer such as St and IBVE via a radical polymerization mechanism. If the iniferter technique described above can be applied to these alternating copolymerization systems, the block copolymers containing an alternating copolymer sequence are expected to be synthesized efficiently.

To prepare mono-, bi-, and tetrafunctional polymeric photoiniferters consisting of alternating copolymer sequences, the alternating copolymerizations of St with DEF or DiPF in the presence of BDC, XDC, and DDC were carried out in benzene at 30°C. The resulting copolymeric photoiniferters were then used for alternating copolymerization of IBVE with MAn. The results are shown in Table II, in which copolymers obtained by BDC-PSt and XDC-PSt systems are also indicated.

The alternating copolymers thus obtained were hydrolyzed with 5% sodium hydroxide aqueous solution. During hydrolysis, the whole polymers dissolved. Since the alternating copolymers of St-

with DEF or DiPF us
ferters were not hydrolyzed
the copolymers unreacted
block copolymers obtained
organic solvents, but t
anol and water.

To confirm further copolymers, the GPC obtained from alternatin and MAn with BDC ferter were observed sults are shown in Fig (RI detector) of the p molecular weight side photoiniferter [P(St Similar results were a curve using UV det Therefore, it is clea consisting of P(St- MAn) was produced

From Table II, the observed yields were the same as that obtained with copolymeric photoinitiators containing allyl groups, the following polymers might be prepared.

Table II. Results of alternating compolymerization of IBVE with MAn in the presence of polymeric photoinitiaters^a

Polymeric photoiniferter ^b	Second monomers		Time h	Total yield g	Fractions isolated/wt%		
	MAN (M ₃)	IBVE (M ₄)			PM ₁ or alt-P(M ₁ —M ₂)	Alt- P(M ₃ —M ₄)	Block copolymer
M ₁ —M ₂	g	g	ml	—	—	—	—
None	—	2.0	2.0	6	0.24	—	—
BDC-PSt	(0.2)	2.0	2.0	6	0.68	0	42.2
XDC-PSt	(0.2)	2.0	2.0	6	1.14	0	30.6
BDC-P(St-DEF)	(0.3)	2.0	2.0	8	1.40	0	21.0
XDC-P(St-DEF)	(0.3)	2.0	2.0	8	1.53	0	20.3
BDC-P(St-DiPF)	(0.2)	1.0	1.0	4	0.54	7.8	28.7
XDC-P(St-DiPF)	(0.2)	1.0	1.0	4	0.64	5.9	24.3
DDC-P(St-DiPF)	(0.2)	1.0	1.0	4	1.84	0	23.7
							76.3 ^c

Photopolymerized in benzene at 30°C.

^b All copolymers consisted of alternating 50:50 (in mol%) composition.

- c Cross-linked polymer was produced.

where M_1 , M_2 , M_3
IBVE, and $MA_{\text{p},r}$

As described above, the inferters with alternating blocks of alternating copolymers are obtained by DDC polymerization, the alternating copolymers being formed by the polymerization of the monomers in the inferters proceeding sequentially in a linked block copolymer.

The ABA block DiPF) with P(IVB)

copolymerization pro-
the initiator systems
and the polymers having
1 bonds at their chain
are similar to the present

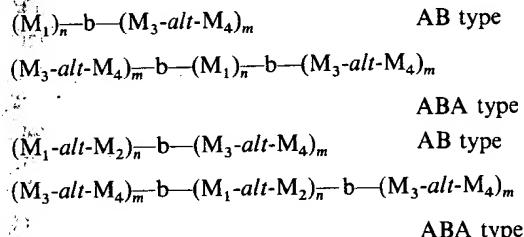
at the electron-accept-
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with DEF or DiPF used as copolymeric photoiniferters were not hydrolyzed under these conditions, the copolymers unreacted were not present. The block copolymers obtained were not soluble in most organic solvents, but they were dispersed in methanol and water.

To confirm further the formation of the block copolymers, the GPC curves for the polymer obtained from alternating copolymerization of IBVE and MAn with BDC-P(St-*alt*-DiPF) as photoiniferter were observed in tetrahydrofuran. The results are shown in Figure 5. The GPC elution curve (RI detector) of the polymer was shifted to higher molecular weight side than that of the copolymeric photoiniferter [P(St-*alt*-DiPF)] initially used. Similar results were also observed for GPC elution curve using UV detector (λ_{254} nm for St unit). Therefore, it is clear that the block copolymer consisting of P(St-*alt*-DiPF) with P(IBVE-*alt*-MAn) was produced by these iniferter technique.

From Table II, the block copolymers were confirmed to be synthesized in high yields, and their observed yields were in the order; mono- < bi- < tetra-, with respect to the functionality of the polymeric photoiniferters used. This tendency was the same as that observed for the polymerization with copolymeric photoiniferters (Table I). Therefore, the following AB and ABA block copolymers containing alternating copolymer sequences might be prepared when mono- and bifunctional polymeric photoiniferters were used, respectively.



where M_1 , M_2 , M_3 , and M_4 are St, DEF or DiPF, IBVE, and MAn, respectively.

As described above, since the polymeric photoiniferters with alternating copolymer sequence obtained by DDC are expected to contain star polymer, the alternating copolymerization with these iniferters proceeded with gelation, and the cross-linked block copolymers were produced.

The ABA block copolymer consisting of P(St-*alt*-DiPF) with P(IBVE-*alt*-MAn) was found to show a

Table III. Color changes of the ABA block copolymer consisting of alternating copolymer sequence of P(St-*alt*-DiPF) with P(IBVE-*alt*-MAn) in benzene

Temp/°C	0	25–30	40	60
Color of solution	Blue	Violet	Yellow	Yellowish green

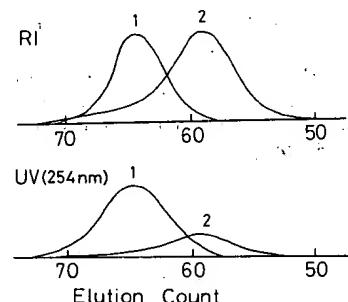


Figure 5. GPC elution counts for the photopolymerization mixture of IBVE and MAn with BDC-P(St-*alt*-DiPF); (1) before and (2) after polymerization. Elution solvent: THF, 1 ml min⁻¹ at 40°C.

thermochromism in benzene. The color changes of its benzene solution with the temperature are shown in Table III. These phenomena seem to be due to a microphase separation of this block copolymer in benzene, and may also give an evidence for the formation of such a block copolymer.

CONCLUSION

As described before, the iniferter technique has been known to give a novel synthetic method for designing of the chain end structure of the producing polymers in radical polymerization. Especially, since some sulfur compounds having *N,N*-diethyldithiocarbamate group were found to serve as excellent photoiniferters and induce living radical polymerization in homogeneous system, these iniferter techniques have been applied to synthesis of various tailor-made polymers such as functional, telechelic, block, and graft polymers.

In this paper, the AB and ABA block copolymers containing random and alternating copolymer sequences were synthesized in high yields through living radical polymerization and copolymerization of vinyl monomers in the presence of mono- and bifunctional polymeric photoiniferters obtained by

Alt- M ₃ –M ₄)	Block copolymer
—	—
42.2	57.8
30.6	69.4
21.0	79.0
20.3	79.7
28.7	63.5
24.3	69.8
23.7	76.3 ^c

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BDC and XDC, respectively.

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ABSTRACT: Thermotropic liquid-crystalline polymers based on polymers bearing mesophatic spacers, have been developed. The type of phase formed by these spacers reduces the interaction between the ester groups and the mesophatic groups.

KEY

The history of mesophatic polymers is a relatively short one. It was predicted that rigid mesophatic polymers would form thermotropic liquid-crystalline solutions at relatively low temperatures. Coincidentally, in the early 1970s, the discovery of a polypeptide, which formed a thermotropic liquid-crystalline solution in solution, was reported. However, little note was given to this discovery until the pioneer work of Dr. J. P. Kennedy and his coworkers in the United States. They synthesized a series of aromatic polyamides containing rigid mesophatic spacers, and found that these polymers formed thermotropic liquid-crystalline solutions at relatively low temperatures. Subsequently, it was found that the rigid mesophatic spacers, which were substituted on the polymer chain, could be substituted on the polymer chain, and that the resulting polymers formed thermotropic liquid-crystalline solutions at relatively low temperatures. This work was followed by a series of patents, which were filed in the United States in the 1970s.⁴

The first report